Silver Nanoparticles Supported by Novel Nickel Metal-Organic Frameworks: An Efficient Heterogeneous Catalyst for an A^3 Coupling Reaction

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Abstract: A novel heterogeneous catalyst of silver nanoparticles was prepared by using a nickel metal-organic framework (Ni-MOF) as a template. The catalyst has a very high catalytic activity and a strict structural selectivity towards linear aliphatic aldehydes in an A^3 coupling reaction. The catalyst could be recovered by simple phase separation and reused for many times without obvious loss of activity.

Key words: silver nanoparticles, template, metal-organic frameworks, heterogeneous catalyst, A^3 coupling

In the past few years, metal-organic frameworks (MOFs) showed a great advantage as an efficient artificial template for the preparation of metal nanoparticles. The distinct advantage of MOFs acting as templates is due to their nanoscale channels or cavities, by which small monodispersed particles are formed instead of the aggregation of nanoparticles into large size.[1] Some recent researches indicated that palladium particles encapsulated on different supporting materials possessed high catalytic activities and good recycle abilities at the same time.[2] Furthermore, some supporting materials have been employed as templates to prepare silver nanoparticles in different forms.[3] However, a heterogeneous catalyst based on MOF-supported silver nanoparticles has not been reported so far.

In the view of consideration above, we designed and synthesized a novel MOF, that is, Ni-MOF,[4] in which there were many free thiophene sulfur atoms from a newly synthesized ligand, H_2DTDC[5] (Figure 1), to provide a suitable template for silver nanoparticles. Furthermore, an A^3 reaction of aldehyde, amine, and alkyne was employed as a model reaction to evaluate the catalytic effect of the constructed heterogeneous catalyst involved silver nanoparticles supported by Ni-MOF.

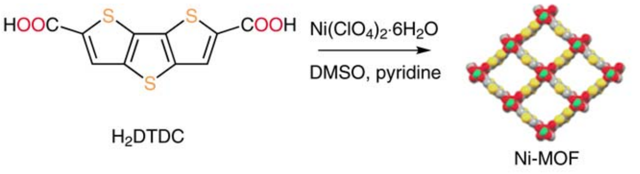

Figure 1 Structure of H_2DTDC and one 2D layer of the novel MOF (Ni-MOF); coloring scheme: C, gray; O, red; S, yellow; Ni, green

It should be noted that, before this investigation, a few templates had been tested in the preparation of heterogeneous silver catalysts in our initial experiments.

Firstly, natural starch was employed as a stabilizer to support silver nanoparticles.[6] However, it was found that for the starch-stabilized Ag catalyst in the A^3 coupling reaction of aldehyde, amine and alkyne, no propargylamine products were observed, suggesting that the silver particles supported by natural starch had no catalytic activities for this A^3 reaction, possibly due to the strong binding affinity between the starch and the silver nanoparticles. Therefore, it is important to select a suitable template with a moderate binding ability to silver nanoparticles.

Secondly, diatomite, a natural porous material, was employed in the catalysis of this A^3 reaction after it was treated with silver nanoparticles (Ag/diatomite).[7] Initially, the reaction of 4-fluorobenzaldehyde with diethylamine and phenylalkyne was used as a model reaction. After the reaction conditions were optimized, the best result was achieved with the reaction temperature of 80 °C, solvent of acetonitrile and catalyst loading of 0.34 mol% (see Supporting Information 1.4). Subsequently, various aldehydes, amines, and alkynes were employed to extend the scope of the reaction substrates. The results were summarized in Table 1.

As shown in Table 1, both aliphatic aldehydes (entries 1–3) and aromatic aldehydes (entries 4–10), as reaction substrates, smoothly afford the corresponding products with moderate to good yields. For the three aliphatic aldehydes, the reaction was finished within shorter time and gave corresponding propargylamines in higher yields in comparison with the aromatic aldehydes, indicating the influence of electronic effect, structural rigidity, and steric hindrance on the A^3 reaction. For examples, the presence of electron-withdrawing groups (F and Br) on the aromatic rings (entries 6 and 7) accelerated the reaction and led to better results than benzaldehyde (entry 4). In contrast, the electron-rich aromatic aldehyde (entry 5) took a longer reaction time to generate the product with a lower yield. In addition, a substituent at the *ortho* position (entry 8) or a substituent with a bigger volume (entry 10), or a heteroatom in an aromatic ring (entry 9) would result in a negative effect on the yield of the coupling reaction.

Being different from starch-stabilized Ag, the Ag/diatomite exhibited a considerable catalytic activity in the A^3 coupling reaction, implying that a suitable template is a

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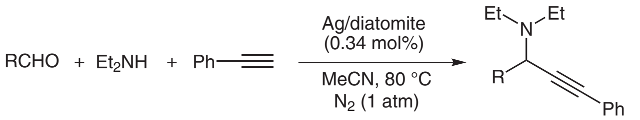
Table 1 Coupling Reaction of Aldehyde, Amine, and Alkyne Catalyzed by Ag/Diatomite[a]



Entry	R	Time (h)	Yield (%)
1	H[b]	3	82
2	$Me(CH_2)_2$	6	74
3	Me_2CH	4	68
4	Ph	11	63
5	4-$MeOC_6H_4$	12	56
6	4-FC_6H_4	6	71
7	4-BrC_6H_4	10	73
8	2-BrC_6H_4	12	51
9	nicotinaldehyde	6	48
10	1-naphthaldehyde	6	47

[a] Conditions: aldehyde (1 mmol), amine (1.2 mmol), and alkyne (1.5 mmol), Ag/diatomite.
[b] $(HCHO)_n$.

crucial point for the performance of a heterogeneous catalyst based on silver nanoparticles.

Subsequently, the recycle of the Ag/diatomite heterogeneous catalyst was estimated in the reaction of polyformaldehyde, diethylamine, and phenylalkyne. A significant decrease of yield (34%) and much longer reaction time (8 h) were observed even for the second run of the Ag/diatomite catalysis. Moreover, it gave only a trace of the final product for the third cycle of the catalysis. The finding suggested that the silver nanoparticles of this catalyst were not immobilized steadily on diatomite. Therefore, the chase for shorter reaction time, higher yields, and good recycle ability of a heterogeneous silver catalyst for the selected A^3 reaction inspired us to attempt the building of Ni-MOF as a template.

Nickel-MOF was synthesized solvothermally through the reaction of H_2DTDC (0.035 mmol) and $Ni(ClO_4)_2{\cdot}6H_2O$ (0.069 mmol) in the presence of DMSO (0.2 mL) and pyridine (0.2 mL). The X-ray analysis showed that the structure of Ni-MOF was a 2D-coordination network crystallizing in the monoclinic space group C2/c (see Supporting Information 2.1). As shown in Figure 1, the dinuclear nickel(II) ions in Ni-MOF were interlinked through the oxygen atoms of DTDC, resulting in many free thiophene-sulfur atoms, which should be helpful for the immobilization of silver nanoparticles.

The synthesis of the silver nanoparticles supported by Ni-MOF was carried out according to a simple process (see Supporting Information 1.2). The TEM images (Figure 2) clearly illustrated the formed silver nanoparticles with a size about 1 nm, which were much smaller than the diatomite-supported silver nanoparticles (see Supporting Information 2.7). The results from UV-vis spectrometry and cyclic voltametry (see Supporting Information 2.4 and 2.5) of Ni-MOF, Ag(I)/Ni-MOF, and Ag/Ni-MOF suggested that the silver ions in Ag(I)/Ni-MOF were completely converted into silver nanoparticles. And XPS analysis showed a 7.03 wt% of Ag in the Ag/Ni-MOF catalyst.

Afterwards, Ag/Ni-MOF was used as a heterogeneous catalyst in the A^3 reaction. Initially, it was used to catalyze the reaction of butyraldehyde with diethylamine and phenylalkyne. After the reaction conditions were optimized, the reaction afforded the corresponding product with a yield of 94% (see entry 4 in Table 2). What is more important, the reaction time was shortened largely to 50 minutes in comparison with six hours of entry 2 in Table 1, as well as with those of the other catalytic systems.[8]

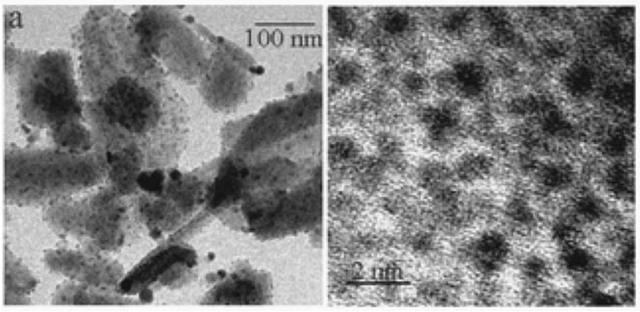


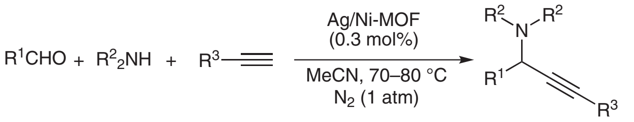
Figure 2 (a) General view of the silver nanoparticles supported by Ni-MOF; (b) HR-TEM image of Ag/Ni-MOF with larger magnification

Subsequently, various aldehydes, amines, and alkynes were applied to extend the scope of reaction substrates.[9] The results are listed in Table 2. From this table, it can be seen that many important and significant phenomena were observed.

First, shapes and sizes of the reaction substrates have a great influence on the reaction. As for the reaction of phenylacetylene with polyformaldehyde and diethylamine (entry 1), in which polyformaldehyde has little steric hindrance, the reaction was finished within ten minutes and generated the corresponding product with a high yield of 95%. With the volume increase of the aldehyde (entry 4) or amine (entry 3), it took longer time to complete the reaction. For the reaction of heptaldehyde with piperidine in the presence of phenylacetylene (entry 10), it took two hours to complete the reaction with a lower yield, perhaps due to their bigger size.

Second, either aromatic aldehydes or branch aliphatic aldehydes hardly gave any reaction products, strongly suggesting the size selectivity of Ni-MOF to reaction substrates. For instance, when the mixture of a linear aliphatic aldehyde and an aromatic aldehydes or a branched aliphatic aldehyde was added to the reaction system, only the corresponding product of a linear aliphatic aldehyde

Table 2 Coupling Reaction of Aldehyde, Amine, and Alkyne Catalyzed by Ag/Ni-MOF[a]



Entry	R^1	R^2	R^3	Time (min)	Yield (%)
1	H[b]	Et	Ph	10	95
2	H[b]	pyrrolidine	Ph	30	93
3	H[b]	piperidine	Ph	30	92
4	$Me(CH_2)_2$	Et	Ph	50	94
5	$Me(CH_2)_2$	pyrrolidine	Ph	60	92
6	$Me(CH_2)_2$	piperidine	Ph	60	94
7	$Me(CH_2)_2$	morpholine	Ph	60	89
8	$Me(CH_2)_5$	Et	Ph	90	86
9	$Me(CH_2)_5$	pyrrolidine	Ph	120	87
10	$Me(CH_2)_5$	piperidine	Ph	120	85
11	H[b]	Et	*n*-Bu	30	92
12	H[b]	piperidine	*n*-Bu	60	90
13	H[b]	morpholine	*n*-Bu	60	88
14	$Me(CH_2)_2$	Et	*n*-Bu	120	82[c]
15	$Me(CH_2)_2$	piperidine	*n*-Bu	120	84[c]
16	$Me(CH_2)_5$	Et	*n*-Bu	120	77[c]
17	$Me(CH_2)_5$	piperidine	*n*-Bu	120	81
18	H[b,d]	Et	Ph	10	94
19	$Me(CH_2)_5$[d]	Et	Ph	90	85
20	H[b,d]	Et	*n*-Bu	30	92
21	$Me(CH_2)_5$[d]	Et	*n*-Bu	120	75
22	H[b,e]	Et	Ph	10	95
23	$Me(CH_2)_5$[e]	Et	Ph	90	87
24	H[b,e]	Et	*n*-Bu	30	90
25	$Me(CH_2)_5$[e]	Et	*n*-Bu	120	78

[a] Conditions: aldehyde (1 mmol), amine (1.2 mmol), and alkyne (1.5 mmol), Ag/Ni-MOF.

[b] $(HCHO)_n$.

[c] Only 0.6 mol% of catalyst was used.

[d] The mixture of 1 mmol of benzaldehyde and 1 mmol of linear aliphatic aldehydes. Only the corresponding products of linear aliphatic aldehydes were obtained.

[e] The mixture of 1 mmol of isobutyraldehyde and 1 mmol of linear aliphatic aldehydes. Only the products of linear aliphatic aldehydes were obtained.

was detected (entries 18–25). Therefore, the strict structural selectivity of the Ni-MOF template to linear aliphatic aldehydes implies that Ag/Ni-MOF could be a potential candidate for the use of separation between linear aliphatic aldehydes and aromatic or branch aliphatic aldehydes.

Third, the presence of a bulky alkyl or aryl group on the alkyne moiety also affected the reaction. When hexyne was selected as a reaction substrate, the reactions were experienced in longer time with lower yields (entries 11–17) in comparison with the phenylacetylene reactions. This indicated that phenylacetylene had a higher reactivity than hexyne in this reaction.

It should be stressed that the reaction time of the A^3 coupling catalyzed by Ag/Ni-MOF was shortened largely in comparison with the catalytic results previously reported,[8] indicating that the silver nanoparticles supported by Ni-MOF has an excellent reactivity due to a larger interaction area resulted from the unique environment of the silver nanoparticles on/in Ni-MOF.

Table 3 Recycling of Ag/Ni-MOF[a]

No. of cycles	Run 1	Run 2	Run 3	Run 4	Run 5
Yield (%)[b]	95	96	94	95	93
Time (min)	10	10	10	15	15

[a] Reaction conditions: $(HCHO)_n$ (1 mmol), Et_2NH (1.2 mmol), phenylacetylene (1.5 mmol), Ag/Ni-MOF (0.3 mol%), MeCN, 75 °C, nitrogen (1 atm).

[b] Isolated yield.

Furthermore, the recycle ability of the Ag/Ni-MOF catalyst was investigated. As shown in Table 3, the heterogeneous catalyst could be reused several times without obvious loss in catalytic activity. Even in the fifth round, a good yield of the reaction product still can be achieved by slightly prolonging the reaction time.

In summary, a heterogeneous catalyst of silver nanoparticles was prepared via the selection of supporting templates. The experimental results showed that the moderate binding affinity between template and nanoparticles, as well as the size of the nanoparticles supported on the template, is a key factor for the catalytic efficiency of a heterogeneous catalyst. Furthermore, the good selectivity of the Ni-MOF template to linear aliphatic aldehydes implies that Ag/Ni-MOF could be a potential candidate for the use of separation between linear aliphatic aldehydes and aromatic or branch aliphatic aldehydes. By means of metal-organic frameworks, we can design and adjust the void cavities and coordination atoms to nanoparticles. This preparation provides us a new method to design and synthesize heterogeneous catalysts and to develop the catalysis of metal nanoparticles. The application of the constructed heterogeneous catalyst for other organic reactions is in progress in our laboratory.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

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(4) X-ray diffraction data of Ni-MOF were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mn Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct method.[10]
Crystallographic Parameters
$C_{40}H_{34}N_4Ni_2O_{13}S_6$, M = 1088.49, monoclinic, space group C2/c, a = 22.7475, b = 19.5874, c = 12.0742 Å, a = 90.000°, b = 99.593°, g = 90.000°, V = 5304.318 Å^3, Z = 4, D_c = 1.363 g/cm^3, F(000) = 2232, m = 1.004 mm^{-1}, crystal size: 0.161 × 0.088 × 0.066, goodness of fit: 0.914, R_1[I > 2σ(I)] = 0.0677, wR_2[I > 2σ(I)] = 0.1742, R_1 (all data) = 0.1275, wR_2 (all data) = 0.2036, residuals (e Å^{-3}): 0.546, –0.648. CCDC 675102.

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(9) **General Procedure for the A^3 Coupling Reaction**
To a solution of aldehyde (1.0 mmol) and amine (1.2 mmol) in MeCN (5.0 mL) was added a certain loading of catalyst (5.0 mg). Then the mixture was degassed in vacuum and put into a nitrogen atmosphere. After adding alkyne (1.5 mmol) into the mixture, it was heated at 70–80 °C for a required reaction time. Then the solid phase was filtered off and residue solvent was evaporated under vacuum. Product was obtained after purification by column chromatography.

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