Cobalt-Containing Mesoporous ZSM-5 Zeolite Catalyzed C=C Bond Cleavage of Alkenes To Form Nitriles

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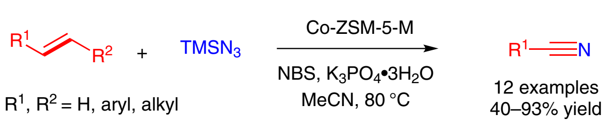

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Abstract Cobalt-containing mesoporous ZSM-5 zeolite (Co-ZSM-5-M) catalyst showed high catalytic activity, selectivity, and excellent reusability in C=C double-bond cleavage of alkenes to form aromatic nitriles. All reactions proceeded smoothly to afford the desired target products in moderate to high yields under the optimal conditions. The Co-ZSM-5-M catalyst was recycled up to at least seven consecutive cycles without significant loss of its catalytic performance.

Key words mesoporous zeolite, Co-ZSM-5-M, C=C bond cleavage, alkene, nitrile

Nitriles are among the most prominent targets in synthetic chemistry because of their biological and pharmaceutical activities.[1] Moreover, the cyano group is a key precursor for multifunctional groups including aldehydes, amines, amidines, amides, or carboxylic acids.[2] Generally, Sandmeyer or Rosenmund–von Braun reaction approaches are traditional methods for the preparation of nitriles.[3] In the past decades, a metal-mediated approach has also been investigated in the coupling of aryl (pseudo)halides or aryl boric acid with metal cyano reagents such as MCN (M = K, Na, Cu, or Zn), TMSCN, or $K_3Fe(CN)_6$.[4] Recently, transition-metal-catalyzed C–H functionalization reactions have been widely developed as a powerful tool for the cyanation.[5] More recently, the group of Guo,[6] Denton,[7] and Chow[8] discovered efficient nitrogenation reaction of alkenes through C=C bond cleavage to produce diverse aromatic nitriles. Especially, Jiao and co-workers described novel *N*-bromosuccinimide (NBS)-mediated nitrile synthesis through C=C bond cleavage of aromatic styrenes.[9] However, these methods suffered from harsh reaction conditions, bad functional-group compatibility, prefunctionalization of the starting materials, and the difficulty of separation of homogeneous catalysts from the reaction products. Therefore, the development of a recyclable and practical catalyst with high activity and recyclability under mild conditions to achieve this transformation is a great challenge. Herein we first report the direct nitrogenation reaction of alkenes to prepare aromatic nitriles over Co-ZSM-5-M catalyst in high yield. The highly dispersed cobalt species in the Co-ZSM-5-M framework have high activity, and the mesoporosity in the catalyst facilitates the mass transfer and therefore improves its catalytic performance. In addition, the Co-ZSM-5-M catalyst can recycle seven runs without any significant activity loss.

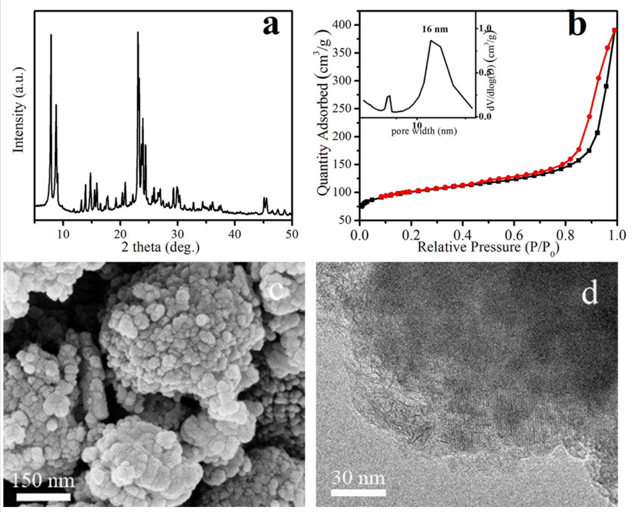


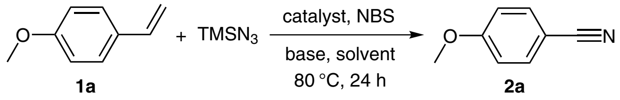
Figure 1 (a) The XRD pattern of Co-ZSM-5-M, (b) N_2 adsorption isotherm of the Co-ZSM-5-M sample, (c) SEM and (d) TEM micrographs of Co-ZSM-5-M.

Figure 1 (a) shows the XRD pattern of the Co-ZSM-5-M, which exhibits typical peaks in the range of 5–50° associated with the MFI structure. The inductively coupled plasma (ICP) analysis clearly points out the cobalt content of 2.4 wt% in the Co-ZSM-5-M, which suggests that the cobalt has been successfully introduced into the zeolite. The nitrogen sorption isotherm of the Co-ZSM-5-M exhibits a hysteresis loop at a relative pressure of 0.5–0.95, which is typically assigned to the presence of a mesostructure (Figure 1, b). Correspondingly, the mesopore size diameter is centered at 16 nm (insert, Figure 1, b). Sample textural parameters are presented in the Supporting Information. The scanning electron microscopy (SEM) image reveals the Co-ZSM-5-M sample with a particle size in the range of 300–600 nm. It seems that the particle is composed of the aggregation of the nanoparticles with main size of 15–40 nm (Figure 1, c). Transmission electron microscopy (TEM) imaging indicates that the cobalt particles are dispersed in the Co-ZSM-5-M.

In order to explore this approach, 4-methoxystyrene (**1a**) was chosen as a model substrate to react with $TMSN_3$ (Table 1). First, the reactions were performed with different transition-metal catalysts. It was found that $Cu(OAc)_2$ and $Co(acac)_2$ afforded lower yields compared to $Co(NO_3)_2{\cdot}6H_2O$ (Table 1, entries 1–3). Much better results were provided by 50 mg Co-ZSM-5-M, which induced a complete nitrogenation of the substrate and gave **2a** in 93% yield (Table 1, entry 4). Further investigation revealed that the base played a critical role in this transformation, and the $K_3PO_4{\cdot}3H_2O$ was superior to other bases, such as KOH, K_2CO_3, and KF (Table 1, entries 5–7). Screening a range of solvents displayed that acetonitrile (MeCN) performed best among other solvents including tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and toluene (Table 1, entries 8–10). In addition, the use of ZSM-5 zeolite (no cobalt incorporation) as the catalyst was less effective (Table 1, entry 11). This control experiment indicated that the incorporation of cobalt is the key for generating catalytic activity.

With the optimized conditions in hand (Table 1, entry 4), we next turned our attention to evaluate the scope of nitrogenation reaction of alkenes. As shown in Scheme 1, the examined substrates provided moderate to excellent yields. Generally, common substituents including electron-donating groups were all tolerated under the standard conditions, giving the corresponding products **2a–f** in good to excellent yields. Notably, styrene also proceeded smoothly to provide the benzonitrile **2g** in moderate yield. Moreover, alkenes with 2-thienyl and the sterically hindered 1-naphthyl group afforded the corresponding nitriles **2h** and **2i** in 75% and 68% yields, respectively. It is noted that 1,2-disubstituted alkene could obtain the aromatic nitriles **2j** and **2k** in 54% and 48% yields, which tremendously expand the scope of this nitrogenation reaction. Furthermore, 1-ethynyl-4-methoxybenzene (**1l**) also gave the desired product **2l** in 40% yield.

Table 1 Optimization of Reaction Conditions in the C=C Bond Cleavage of Alkene **1a** to Prepare Nitrile **2a**[a]



Entry	Catalyst	Base	Solvent	Yield (%)[a,b]
1[c]	$Cu(OAc)_2$	$K_3PO_4{\cdot}3H_2O$	MeCN	79
2[c]	$Co(NO_3)_2{\cdot}6H_2O$	$K_3PO_4{\cdot}3H_2O$	MeCN	85
3[c]	$Co(acac)_2$	$K_3PO_4{\cdot}3H_2O$	MeCN	40
4	Co-ZSM-5-M	$K_3PO_4{\cdot}3H_2O$	MeCN	93
5	Co-ZSM-5-M	KOH	MeCN	80
6	Co-ZSM-5-M	K_2CO_3	MeCN	50
7	Co-ZSM-5-M	KF	MeCN	78
8	Co-ZSM-5-M	$K_3PO_4{\cdot}3H_2O$	THF	<5
9	Co-ZSM-5-M	$K_3PO_4{\cdot}3H_2O$	toluene	<5
10	Co-ZSM-5-M	$K_3PO_4{\cdot}3H_2O$	DMF	67
11	ZSM-5-M	$K_3PO_4{\cdot}3H_2O$	MeCN	48

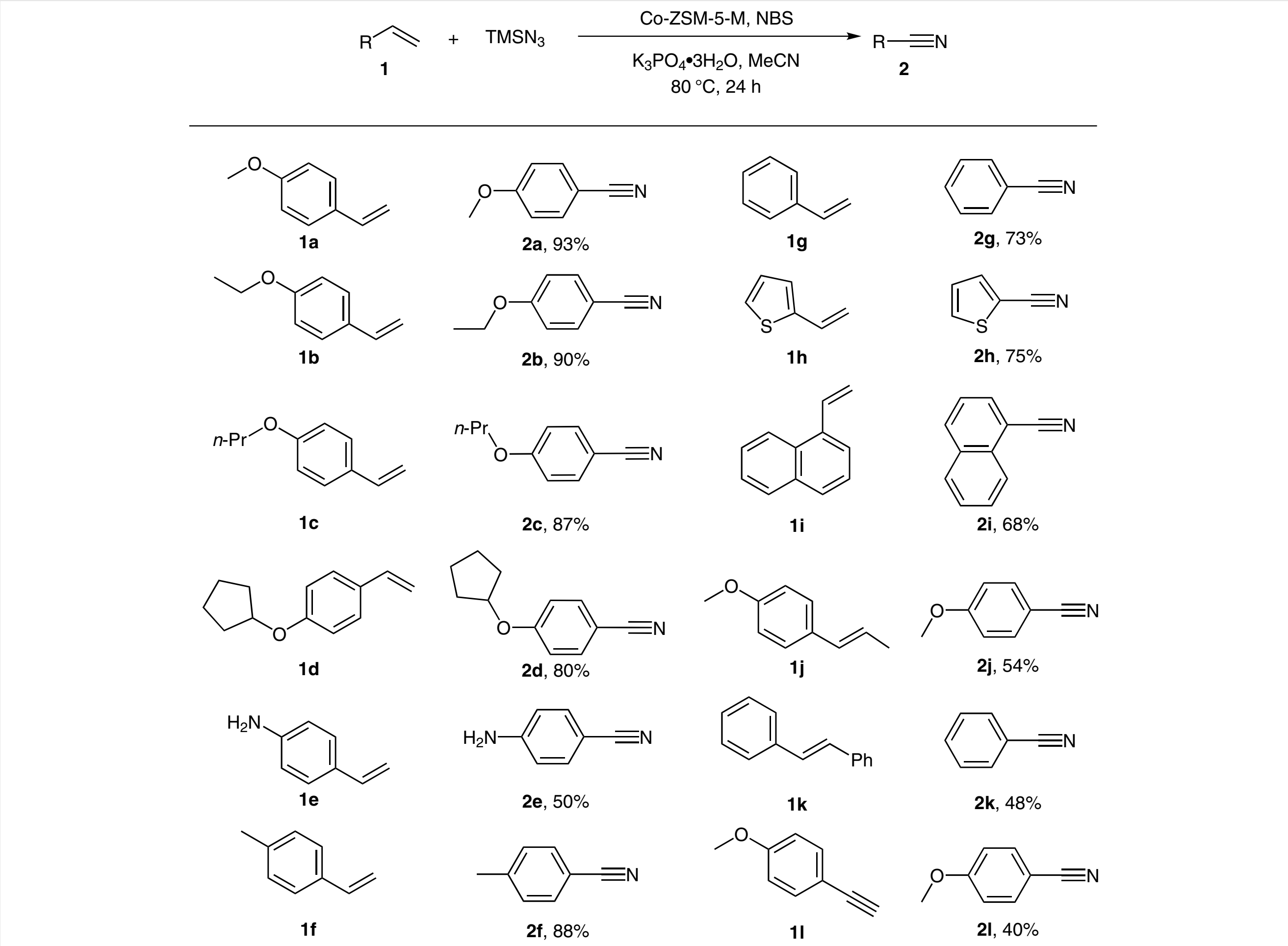
[a] Co-ZSM-5-M (50 mg), base (2.0 equiv), NBS (1.0 equiv), $TMSN_3$ (2.5 equiv).
[b] Yields were determined by GC.
[c] Conditions: 10 mol% catalyst were used.

The recyclability of the Co-ZSM-5-M catalyst was tested in the C=C bond cleavage of 4-methoxystyrene with $TMSN_3$. Table 2 shows the recyclable results under the adopted reaction conditions. After each run, the Co-ZSM-5-M catalyst was separated from the product by centrifugation and was immediately reused (with the addition of fresh reactants) without any treatment. The Co-ZSM-5-M catalyst can recycle seven runs without significant reduction in activity. This result indicates that the Co-ZSM-5-M zeolite possesses a good reusability, which is one of the key features in the practical application in industry.

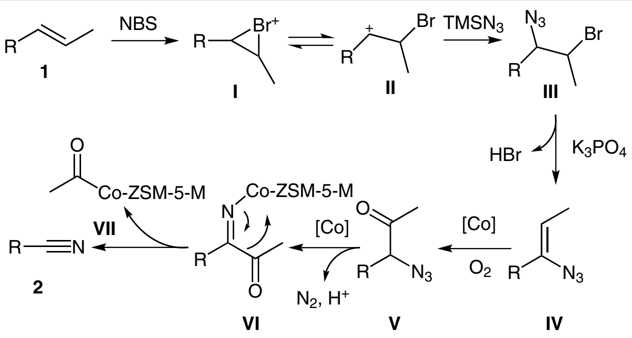
Table 2 Catalyst Recyclability Experiment[a]

Entry	Co-ZSM-5-M[b]	Yield (%)
1	1st cycle	93
2	2nd cycle	93
3	3rd cycle	92
4	4th cycle	90
5	5th cycle	90
6	6th cycle	89
7	7th cycle	89

[a] GC yield, **1a** was used as the substrate.
[b] Fresh Co-ZSM-5-M was used in the first cycle, and then the catalyst was directly used in the following cycles after being recovered.



Scheme 1 The scope of reaction and yields were determined by GC



Scheme 2 Proposed reaction pathway

On the basis of these results and related precedents,[9,10] a plausible reaction mechanism for this Co-ZSM-5-M-catalyzed C=C bond cleavage of alkenes to form nitriles is thus proposed (Scheme 2). First, alkene **1** reacts with NBS producing a bromonium ion **I**, which could undergo isomerization to intermediate **II**, which is subsequently attacked by azide ions to generate species **III**. In this case, the intermediate **III** undergoes elimination assisted by K_3PO_4 to form the alkenylazide intermediate **IV**. The following oxidization of **IV** affords intermediate **V** by the cobalt catalyst. Subsequently, the intermediate **V** gives imidoyl cobalt intermediate **VI** by the Co-ZSM-5-M catalyst via the denitrogenative process. Finally, the following carbon–carbon bond cleavage and rearrangement of **VI** generates the desired products **2** and complex **VII**.

In summary, we have described Co-ZSM-5-M zeolites as a useful catalyst for aromatic nitriles synthesis from alkenes through C=C bond cleavage.[11] The experiments demonstrated that the Co-ZSM-5-M exhibited good catalytic activity and selectivity in this transformation. This reaction provides a series of aromatic nitriles synthesized with this method in moderate to excellent yields. Further investigation is being conducted to explain the reaction mechanism on mesoporous Co-ZSM-5 zeolites.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560662.

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(11) **General Procedure for the Preparation of Aromatic Nitriles – Typical Procedure for Compound 2a**

To the mixture of **1a** (190 mg, 1.0 mmol), $TMSN_3$ (222 mg, 2.5 mmol), NBS, $K_3PO_4{\cdot}3H_2O$ (251 mg, 2.0 mmol) in MeCN (2.0 mL) was added Co-ZSM-5-M (50 mg) in one portion at r.t. The reaction mixture was heated to 80 °C and stirred for 2 h, until the substrate **1a** was consumed as indicated by TLC. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: PE–EtOAc, 30:1) to afford product **2a** (99 mg, 86% yield).

4-Methoxybenzonitrile (2a)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, J = 9.0 Hz, 2 H), 6.96 (d, J = 9.0 Hz, 2 H), 3.86 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8, 133.9, 119.1, 114.7, 103.9, 55.5.

4-Propoxybenzonitrile (2c)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, J = 9.0 Hz, 2 H), 6.94 (d, J = 9.0 Hz, 2 H), 3.96 (t, J = 6.5 Hz, 2 H), 1.89–1.76 (m, 2 H), 1.04 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 133.9, 119.2, 115.1, 103.6, 69.8, 22.3, 10.3.

4-(Cyclopentyloxy)benzonitrile (2d)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, J = 9.0 Hz, 2 H), 6.91 (d, J = 9.0 Hz, 2 H), 4.84–4.73 (m, 1 H), 1.98–1.88 (m, 2 H), 1.88–1.74 (m, 4 H), 1.70–1.57 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.5, 149.9, 146.9, 124.0, 121.6, 64.1, 55.6, 51.2, 34.5.