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Cobalt on Mesoporous Silica: The First Heterogeneous Pauson−Khand Catalyst

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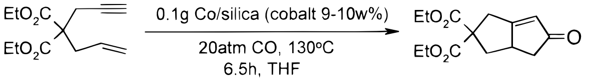
Cycloaddition of alkynes with alkenes and carbon monoxide by dicobalt octacarbonyl to cyclopentenones (known as Pauson−Khand reaction) has been recognized as one of the most important methodologies to synthesize cyclopentenone derivatives.[1] Recently the catalytic version of the Pauson−Khand reaction has been developed by us and others.[2] In developing large-scale processes, it is extremely important to heterogenize homogeneous catalyst systems, because heterogeneous catalytic systems have many advantages over homogeneous counterparts in liquid-phase reactions, including easy removal of catalysts from reaction mixtures and recycling/reuse of catalysts.[3] In heterogenizing homogeneous catalyst systems, supports such as polymers, silica, and zeolites have received the most attention.[4] Recently, various mesoporous silicas with pore size ranging from 2 to 10 nm have been extensively applied as supports for many catalytically active metals and homogeneous catalysts.[5] Here we report the first heterogeneous catalyst system for Pauson−Khand reactions. The catalyst system is metallic cobalt supported on mesoporous silica. The catalyst is air-stable and reusable, and exhibits an excellent catalytic performance for many intramolecular Pauson−Khand reactions.

Table 1. Intramolecular Pauson−Khand Reaction Catalyzed by Various Catalytic Systems[a]

entry	catalyst	time (h)	yield (%)[b]
1	Co/SBA-15	6.5	95
2[c]	$Co_2(CO)_8$	4	93
3	recoved from #1	6.5	98
4	recoved from #3	6.5	98
5	recoved from #4	6.5	98
6[d]	Co/SBA-15	6.5	18
7[e]	Co/SBA-15	18	9
8	Co/SBA-15[f]	6.5	95
9	cobalt oxide/SBA-15	6.5	N.R.[g]
10	Co/MCM-41	6.5	98
11	Co/A-Silca gel	23	83

[a] Reaction conditions: 0.1 g of cobalt on silicas (cobalt 9−10 wt %), 1.26 mmol allylpropargyl diethylmalonate,130 °C, CH_2Cl_2, 20 atm of CO pressure. [b] Isolated yield. [c] 27.5 mg of $Co_2(CO)_8$ was used. [d] 15 atm of CO. [e] 110 °C. [f] Prepared by the conventional impregnation method. [g] No reaction.

Cobalt metal has been deposited on mesoporous silica supports, SBA-15 and MCM-41,[5] by decomposing $Co_2(CO)_8$ in a refluxing toluene solution. The infrared spectroscopic data of the supported catalysts demonstrated the absence of carbonyl vibration, confirming a complete decomposition of metal carbonyls. Cobalt loading was adjusted to 9−10 wt %. X-ray powder diffraction (XRD) patterns of the supported catalysts revealed face centered cubic (fcc) and hexagonal close packed (hcp) metallic cobalt peaks. No cobalt oxide peak was observed in the XRD. The following intramolecular Pauson−Khand reaction of enyne has been investigated as a test reaction (eq 1).



(1)

Table 1 summarizes the results of the reaction using various heterogeneous cobalt catalysts. Entry 1 shows that cobalt supported on mesoporous SBA-15 silica (Co/SBA-15) is very active with a 95% isolated yield, which is comparable to that of $Co_2(CO)_8$ (entry 2 in Table 1). Heterogeneous catalysts often suffer extensive leaching of active metal species during reactions and eventually lose their catalytic activity. To our surprise, Co/SBA-15 catalysts maintained their high catalytic activity even after four recyclings and reuse of the catalyst (entries 3−5 in Table 1). The FT-IR measurement and the elemental analysis (by ICP-AES) of the reaction mixture after conducting the reaction showed that no cobalt species was leached out. When either the reaction temperature or CO pressure was lowered, the activity of the catalyst decreased significantly (entries 6 and 7 in Table 1). Thus, to keep a high catalytic activity, the reaction temperature and CO temperature have to be at least 130 °C and 20 atm, respectively.

Cobalt metal was also loaded onto SBA-15 using the conventional impregnation method.[6] The catalytic activity of the impregnated catalyst was also very good (entry 8 in Table 1). This result has important meaning to the future large-scale application of the catalyst because cheap cobalt nitrate instead of expensive $Co_2(CO)_8$ can be used as a cobalt precursor. Cobalt

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(6) The impregnated Co/SBA-15 catalyst was prepared by the calcination of impregnated cobalt nitrate followed by reduction at 650 °C under hydrogen atmosphere. X-ray powder diffraction pattern of the catalyst showed that most of cobalt species are metallic but still a small fraction of cobalt oxide was left.

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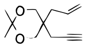
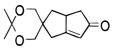
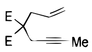
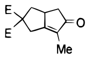
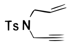
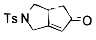
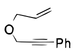
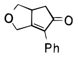
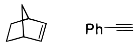
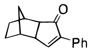
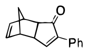
Table 2. Pauson−Khand Reaction Catalyzed by Co/SBA-15[a]

entry	substrate	product	time(h)	yield(%)[b]
1			6.5	96
2			18	92
3			6.5	88
4			18	98
5			6.5	11[c]
6			6.5	36[c]

[a] Reaction conditions: 0.1 g of Co/BSA-15 (cobalt 9−10 w%), 1.26 mmol of substrate, 130 °C, CH_2Cl_2, 20 atm of CO. [b] Isolated yield. [c] Aromatic compound was isolated.

oxide supported on SBA-15 exhibited no catalytic activity (entry 9 in Table 1).

Amorphous silica gel (Merck 60F254, surface area 344 m^2/g) and most popular mesoporous silica MCM-41 (surface area of 940 m^2/g and mean pore size of 3.5 nm) have also been applied as supports (entries 10 and 11 in Table 1). Clearly the catalytic performance of Co/SBA-15 and Co/MCM-41 is superior to that of Co/amorphous-silica. The higher catalytic activity of mesoporous supported catalysts might result from the easy access and confinement of substrates in regular mesopores.

To demonstrate the versatility of Co/SBA-15 catalyst, we have screened various substrates for Pauson−Khand reactions (Table 2). The reaction proceeded smoothly in the intramolecular manner with monosubstituted olefines regardless of the substitution pattern of alkynes (entries 1 and 2), although the internal alkyne substrate needs a relatively long reaction time. Heteroatom bridged enynes produced azabicyclic compound (entry 3) and oxobicyclic compound (entry 4) from the corresponding substrates in good yields. The catalyst has been tested for intermolcular cycloaddition reaction (entries 5 and 6). The catalytic performance of Co/SBA-15 catalyst for intermolecular reactions was not as good as that for intramolecular reactions. The expected cycloaddition products were obtained in low yields with a concomitant formation of [2+2+2] cycloaddition product. Interestingly, norbornadiene was a better substrate than norbornylene, presumably due to the number of double bonds. So far, the mechanism of the heterogeneous catalytic Pauson−Khand reaction has not been elucidated. The adsorption of CO and substrate on cobalt metal surface followed by the insertion of CO and cyclization might produce cyclopentenones.[7]

In conclusion, we have developed new active heterogeneous Pauson−Khand catalysts using cobalt metal supported on mesoporous silica. The catalyst systems are air-stable and reusable, and quite effective for many intramolecular cycloaddition reactions. In addition, important features of the catalytic reaction are an experimental simplicity and a high conversion rate. Application of the new catalytic system systems to other cycloaddition reactions is now in progress.

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