

Synthesis and Characterization of the Surface Modified SBA-15 with Dicobaltcarbonyl Complex

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Cobalt-immobilized SBA-15 **6a-c** was synthesized from alkyne-attached SBA **5a-c** by the reaction with $\text{Co}_2(\text{CO})_8$ in toluene. Alkyne group was introduced into amino SBA-15 (**4**) by imine-linkage or substitution with propargyl bromide to afford iminoalkyne **5a** and aminoalkyne **5b**, respectively. Meanwhile, alkyne **5c** was prepared in one-step by reacting triethoxysilyl hexyne with SBA-15. Dicobalt-complexes **6a-c** were characterized by means of FT-IR, solid-state NMR and elemental analysis.

Key Words : Alkyne, Cobalt complex, Mesoporous SBA-15, Immobilization

Introduction

Diverse physicochemical properties of cobalt complexes relied on the oxidation state or the ligands on-bound have led their applications into the catalytic Fisher-Tropsche¹ and Pauson-Kahand² reactions, as electromagnetic materials³ and electrolyte in dye sensitized solar cell.⁴ For an efficient performance of cobalt catalyst, a delocalized distribution of cobalt atoms on a supporting material is one of crucial requirement because it provides a sufficient contacting area with the substrate. Various techniques for the incorporation of cobalt catalyst into silicate have been reported; adsorption method,⁵ wet impregnation method,⁶ template-ion exchange,⁷ and pH-adjusting method.⁸ Each method is of practical advantage or disadvantage in usage particularly in acidic or basic medium and for the control of porosity. None of these processes, however, is satisfactory for non-localized dispersion of catalyst into porous support.

Calcination of the silicate after covalent conjugation of cobalt complex is considered as one of the way for a dispersion of cobalt catalyst in preserving distance between each cobalt atoms. With mind these aspect, we incorporated cobalt atoms into SBA-15, representative mesoporous silica, by the alkyne-cobalt complex formation. SBA-15 was initially silanized with appropriate alkoxy silane molecules to form amino-, imino- and aliphatic-alkyne **5a-c** then reacted with dicobaltoctacarbonyl to afford cobalt-SBA complex **6a-c**. Here, we report the synthesis and characterization of these complexes.

Experimental

General Information. All reactions were carried out under atmospheric N_2 pressure. THF was dried by distillation with sodium-benzophenone. Toluene was distilled with P_2O_5 . FT-

IR spectroscopic data was collected with KBr pellets on a Prestige-21 IR (Shimadzu). For solution-state NMR data, Gemini 200 MHz (Varian); for solid-state NMR, ^{13}C MAS (magic angle spin)/CP (cross polarization) NMR (Varian, Unity-Inova 200) were used, respectively. SEM data were collected from AIS2100 (Mirero Inc., Korea), and Elemental analysis was performed using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Jobin-Yvon Ultima C) at Korea Research Institute of Chemical Technology.

Synthesis.

Amino-SBA-15 (4): To a solution of SBA-15⁹ (1 g) in toluene (20 mL) was added aminopropyltriethoxysilane (APTES, 500 mg, 2.26 mmol) and heated at 100 °C for 24 h under dry N_2 atmosphere. The solid silicate was filtered and washed with toluene and ethanol. Residual organic materials were removed using Soxhlet extractor refluxing in toluene. Further drying and evaporation under reduced pressure gave SBA(**4**) (850 mg). TGA analysis: 0.6 mmol of APTES per gram of silicate **4**; FT-IR ν_{max} (KBr)/ cm^{-1} 3452 (NH_2 stretching), 2931 (CH_2), 1643 (NH_2 bending), 1468 (C-N), 1076 (Si-O-Si), 961 (Si-OH), 799 (Si-O), 459 (Si-O); ^{13}C -MAS NMR (200 MHz, CDCl_3) δ 9.6 (Si- CH_2), 21.4 (CH_2), 43.3 (CH_2 - NH_2).

Imino-alkyne (5a): A mixture of amino-SBA **4** (500 mg, 0.3 mmol NH_2), 4-ethynylbenzaldehyde (59 mg, 0.45 mmol) and trimethylorthoformate (48 mg, 0.45 mmol) in ethanol (10 mL) was heated at 60 °C for 24 h. The reaction mixture was filtrated, washed with ethyl acetate and ethanol to give yellow powder. Refluxing in Soxhlet extractor and drying in vacuum oven at 100 °C afforded yellowish silicate **5a** (485 mg). FT-IR ν_{max} (KBr)/ cm^{-1} 3308 ($\equiv\text{CH}$), 2942 (CH_2), 2106 ($\text{C}\equiv\text{C}$), 1541 ($\text{C}=\text{N}$), 1085 (Si-O-Si), 800 (Si-O), 464 (Si-O); ^{13}C -MAS NMR (200 MHz, CDCl_3) δ 10.0 (Si- CH_2), 22.0 (CH_2), 42.0 (CH_2 - NH_2), 62.3 ($\equiv\text{C}$ -), 128.5, 131.9 (aryl), 164.1

(C=N).

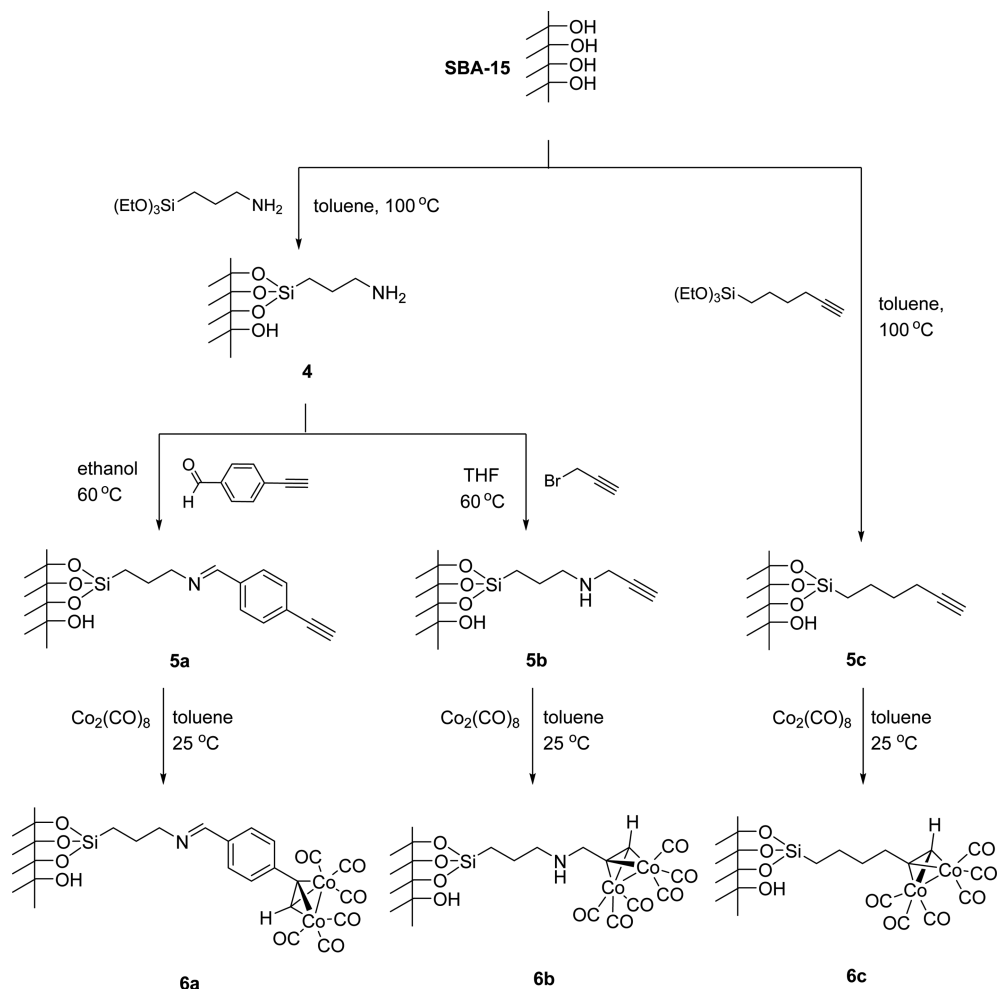
Aminoalkyne SBA-15 (5b): Amino-SBA **4** (500 mg, 0.3 mmol NH₂) was suspended in THF (10 mL) and then propargylbromide (79 mg, 0.66 mmol) and triethylamine (67 mg, 0.66 mmol) were added. After being heated at 60 °C for 24 h, the resulting mixture was filtered, washed with water, ethanol and THF successively to give yellow powder. Soxhlet extraction and drying in vacuum oven at 100 °C afforded yellowish silicate **5b** (450 mg). FT-IR ν_{\max} (KBr)/cm⁻¹ 3301 (\equiv CH), 2948 (CH₂), 2132 (C \equiv C), 1473 (C-N), 1081 (Si-O-Si), 801 (Si-O), 463 (Si-O); ¹³C-MAS NMR (200 MHz, CDCl₃) δ 9.6 (Si-CH₂), 17.4 (-OCH₂CH₃), 21.1 (CH₂), 43.1 (CH₂-NH₂), 59.1 (-OCH₂), 77.8 (\equiv C-).

SBA-15/Silanoalkyne (5c): To a solution of SBA-15 (500 mg) in toluene (10 mL) was added 5-hexynyltriethoxysilane (500 mg, 2.5 mmol). After being heated at 80 °C for 24 h, the reaction mixture was filtered, then washed with toluene and ethanol to give yellow powder. Soxhlet extraction and drying in vacuum oven at 100 °C afforded yellowish silicate **5c** (520 mg). FT-IR ν_{\max} (KBr)/cm⁻¹ 3333 (\equiv CH), 2985 (CH₂), 2118 (C \equiv C), 1081 (Si-O-Si), 806 (Si-O), 458 (Si-O); ¹³C-MAS NMR (200 MHz, CDCl₃) δ 10.1 (Si-CH₂), 17.1 (-OCH₂CH₃), 21.7, 31.7 (CH₂), 59.8 (-OCH₂), 67.7 (\equiv C-), 84.6 (\equiv C-).

Imino-alkyne-cobalt (6a): The solution of imino-SBA **5a** (400 mg, assumed 0.24 mmol alkyne) and dicobalt octacarbonyl (123 mg, 0.36 mmol) in toluene (10 mL) was stirred at room temperature for 1 h. The reaction mixture was filtered, washed with toluene to give brown powder. Soxhlet extraction and drying in vacuum afforded silicate **6a** (320 mg). FT-IR ν_{\max} (KBr)/cm⁻¹ 2970 (CH₂), 2100, 2060, 2033 (CO), 1559 (C=N), 1083 (Si-O-Si), 800 (Si-O), 461 (Si-O).

Amino-alkyne-cobalt (6b): To a solution of dicobalt octacarbonyl (123 mg, 0.36 mmol) in THF (10 mL) was added amino-SBA **5b** (400 mg, 0.24 mmol NH₂) then stirred at room temperature for 1 h. The reaction mixture was filtrated and washed with toluene to give brown powder. Soxhlet extraction and drying in vacuum afforded silicate **6b** (280 mg). FT-IR ν_{\max} (KBr)/cm⁻¹ 2987, 2942 (CH₂), 2094, 2057, 2027 (C=O), 1510 (C-N), 1089 (Si-O-Si), 800 (Si-O), 460 (Si-O).

Silano-alkyne-cobalt (6c): To a solution of dicobalt octacarbonyl (123 mg, 0.36 mmol) in toluene (10 mL) was added SBA **5c** (400 mg) solution then stirred at room temperature for 1 h. The reaction mixture was filtered and washed with toluene to give brown powder. Soxhlet extraction and drying in vacuum afforded silicate **6c** (350 mg). FT-



Scheme 1. Synthesis of alkyne-cobalt immobilized SBA-15 **6a-c**.

IR ν_{\max} (KBr)/ cm^{-1} 2988 (CH_2), 2098, 2056, 2030 (CO), 1078 (Si-O-Si), 809 (Si-O), 459 (Si-O).

Results and Discussion

The cobalt-SBA complexes **6a-c** were prepared from SBA-15 through cobalt complex formation following silanylation as a key step (Scheme 1). To introduce a terminal triple bond into SBA-15, SBA-15 was initially treated with triethoxyaminopropyl silane (TEAPS)⁹ in toluene to give aminoilicate **4**, and then reacted with 4-ethynylbenzaldehyde and 3-bromopropyne, to form **5a** and **5b** respectively. Meanwhile, nitrogen-free SBA-alkyne **5c** was obtained in one-step by the reaction of SBA-15 with triethoxy-6-heptynyl silane in toluene. In notable, the hybrid-SBA **6a-c** was decomposed changing color from dark-brown to grey *via* CO ligands dissociation. Thus, the samples benefit from oxygen-free condition at low temperature (below $-20\text{ }^\circ\text{C}$) for storage.

IR Spectroscopy. For the characterization of SBA-cobalt complexes, a solid-state NMR and IR spectroscopy were used. IR spectra of cobalt-silicate **6a** and $\text{Co}_2(\text{CO})_6$ -5-chloropentyne complex were compared in Figures 1 and 2, respectively. Both $\text{Co}_2(\text{CO})_8$ and $\text{Co}_2(\text{CO})_6$ -5-chloropentyne complexes display three stretching bands around 2000 cm^{-1} assigned to CO ligands (a and c in Figure 1), and $\text{Co}_2(\text{CO})_8$ shows an additional stretching band around 1850 cm^{-1} attributable to bridged CO ligands. Similarly, three peaks representing 6 CO ligands of **6a** appeared near 2000 cm^{-1} characteristically, meanwhile the bridged CO peak near 1850 cm^{-1} disappeared (d in Figure 2). The other intensive peaks are originated from silicates including Si-O ($459, 798\text{ cm}^{-1}$), Si-OH (960 cm^{-1}) and Si-O-Si (1076 cm^{-1}), which additionally support the formation of **6a**, based on the reported data.^{10,11}

Solid-state ^{13}C -NMR. The characterization of intermediates **4** and **5a-c** were confirmed by ^{13}C MAS/CP-NMR and their spectra are shown in Figure 3. We observed the resonance peak for the typical amino methylene group ($\text{H}_2\text{N-CH}_2$) of amino-SBA-15 (**4**) at 43 ppm and the resonance peaks for the silylmethylene groups ($\text{Si-CH}_2\text{CH}_2$ and Si-CH_2) at 24 and 11 ppm. The sp-hybridized carbon of **5a** appeared broadly near 80 ppm, and imine C=N peak was observed at

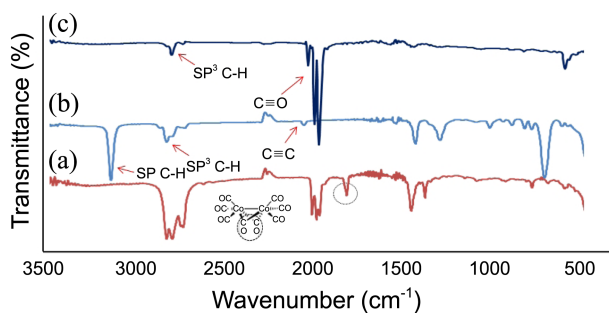


Figure 1. FT-IR spectra of cobalt carbonyl complex with 5-chloropentyne: (a) $\text{Co}_2(\text{CO})_8$, (b) 5-chloropentyne and (c) $\text{Co}_2(\text{CO})_6$ -(5-chloropentyne).

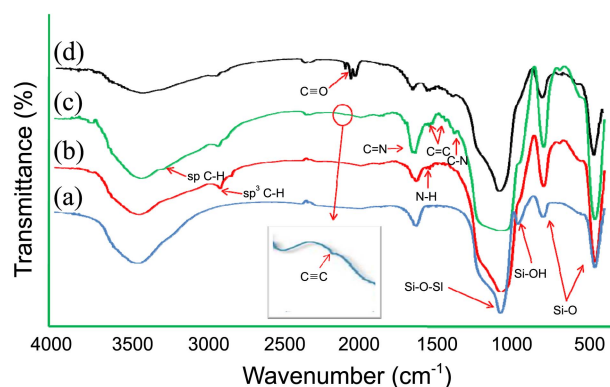


Figure 2. FT-IR spectra of cobalt carbonyl complex on SBA-15: (a) SBA-15, (b) aminosilane **4**, (c) iminoalkyne **5a** and (d) complex **6a**.

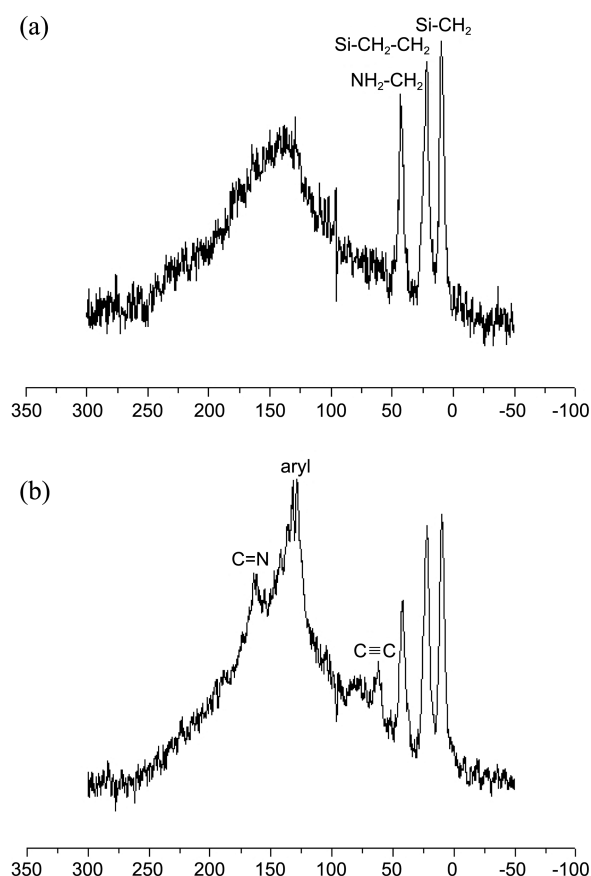


Figure 3. Solid-state ^{13}C -NMR of alkyne attached SBA-15: (a) **4** and (b) **5a**.

$\sim 160\text{ ppm}$. Other carbons bound to silane were assigned by comparison with the literature¹² as in Figure 3. Due to paramagnetic property of cobalt atom, solid-state ^{13}C -NMR peaks of SBA **6a-c** displayed with noise at 100-250 ppm thus CO peaks were hardly observed near 200 ppm.

Elemental Analysis. The elemental compositions of cobalt-SBA **6a** and **6c** were analyzed. Relative ratio and mole numbers of Co, C, H and N atoms are represented in Table 1. The weight ratio of cobalt atom in **6a** and **6c** are 9.01 and 6.57%, respectively. From the mole ratio of $\text{Co/N} = 1.36$ in

Table 1. Relative atomic ratio in cobalt-complexes **6a** and **6c** based in weight % and mole numbers

Compound		C	H	N	Co	Co/N ^a	Co/C ^b
6a	wt %	9.79	1.60	1.54	9.01	5.85 (7.71)	0.92 (0.55)
	Number of moles	0.82	1.60	0.11	0.15	1.36 (2.00)	0.18 (0.11)
6c	wt %	6.44	1.08	–	6.57	–	1.02 (0.82)
	Number of moles	0.54	1.08	–	0.11	–	0.20 (0.17)

^aRatio of cobalt atom to nitrogen. ^bRatio of cobalt atom to carbon. Numbers in parenthesis are theoretical values.

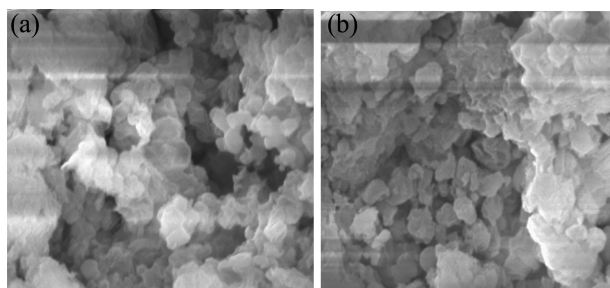


Figure 4. Scanning electron microscopy images: (a) amino-SBA **4**, (b) cobalt-SBA **6a**.

silicate **6a**, 68% of amino groups of aminosilica **4** seems to be converted to the cobalt complex **6a**. The higher mole ratio of Co/C (0.18) than the theoretical (0.11) in SBA **6a** was not clear to be explained. Presumably, it might attribute to the CO ligand dissociation to result. Similarly, SBA **6c** also showed higher cobalt-to-carbon molar ratio (Co/C = 0.20) than the estimation (0.17).

SEM Analysis. The morphology of SBA **4** and **6a** was imaged by SEM as shown in Figure 4. The attachment of bulky alkyne-cobalt complex did not seem to alter 3-dimensional images of SBA-15 from those of intact. As we expected, the coupling of organofunctional motif with silanyl hydroxyl group seemed to be performed under retention of structure ordering of SBA-15.

As summary, we have incorporated cobalt atoms into mesoporous SBA-15 via alkyne-cobalt complex formation. Alkyne group was initially introduced by imine formation with amino SBA-15 **4** or displacement with propargyl-bromide to give iminoalkyne **5a** and aminoalkyne **5b**, respectively. The alkyne functionality was also introduced in one-step by reacting triethoxysilyl hexyne with SBA-15 to afford alkyne **5c**. Reaction with dicobalt octacarbonyl generated alkyne-dicobalt hexacarbonyl complex **6a-c**. This synthetic method could be applied in polymer bead (ASP) and gold surface¹³ to afford cobalt complexes on those surfaces.

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