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Research Article

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Immobilization of acetonitrile ligated cobalt(II) complexes on modified silica and its characterization

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ABSTRACT

Catalyst have played an important role in industry such as energy, pharmaceutical and chemical manufacture since it allows reactions to occur faster at lower temperature. For years, transition metal complexes have been studied intensively as catalyst. In this work, a modified amorphous silica has been studied as support material for cobalt(II) acetonitrile complex through direct and indirect grafting methods. The immobilized materials were characterized by FT-IR, Optic Microscopy, TG-DTA, SEM, and AAS. Furthermore, UV-Vis spectrophotometer was also used to determine electronic absorption of the complexes. In general, either direct or indirect grafting produced grafted material with low leaching grade having less than 10 %. Thermal stability of such complex grafted on the modified silica was moderately high and can be applied until 130 °C. On the other side, based on UV-Vis spectrophotometer the catalyst is better if employed in a water free system.

Keywords: Immobilization, Grafting, Cobalt(II) complex, Modified Silica, Catalyst, Leaching

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INTRODUCTION

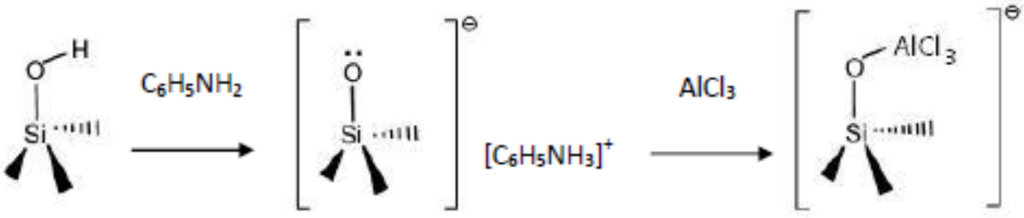
Catalyst have played an important role in industry such as energy, pharmaceutical and chemical manufacture since it allows reactions to occur faster at lower temperature. Catalyst is the most important in synthesis process, either organic or inorganic. There is an interesting to study and modification with the result that catalytic activity and selectivity can be improved and the effect to environment can be reduced.

Transition metal complexes have been studied intensively as catalyst. Chemical properties of the central atoms can influence to reactivity of the complexes [1,2]. Recently, cobalt(II) pthalocianin complex have been immobilized on the surfaces of silica that shown higher chemical stability [3]. Furthermore, cobalt(III) oxide shown good activity and selectivity in both homogeneous and heterogeneous phase compare than other metal oxides [4], as well as nickel and palladium [5]. Homogeneous catalysts have some of problems, such as difficulty in catalyst handling and separation from the reaction system with the result cannot be recycling. On the other side, the accumulation of both transition heavy metals and toxic organic ligands potentially as contaminant in the environment.

Based on economy and environmental issues of the homogeneous catalysts is immobilize homogeneous catalysts on support materials, that is heterogenization of the homogeneous catalysts. Among the various supporting materials available, such as organic support (poly (4-vinylpyridine)) and inorganic support (zeolites, silica, and alumina) [6]. Nowadays, heterogeneous catalysts is the matter needed in the industry, it caused by having several advantages, such as high efficiency, easy to applied in the mediums, simple recycling of the catalysts by filtration, thus considerably decreasing the environmental problems of waste materials [7-8]. In some of cases, immobilization of homogeneous catalyst on the support materials its occur by covalently bonding. This method have been reported enhancing the reactivity and selectivity of the catalyst. Furthermore, the use of weakly or non-coordinating anions

(WCA) as counterions potential in enhancing the reactivity of metal complexes [8-11]. By present of WCA cause the interaction is just form cationic-anionic interactions.

In this work, acetonitrile ligated cobalt(II) complex $[Co(NCCH_3)_6][Cl]_2$ is grafted on the surface of silica modification $(Si\text{-}O\text{-}AlCl_3)^-$ by ionic interaction. To prevent form covalently bond between catalyst $[Co(NCCH_3]^{2+}$ and surface of silica, thus introduced aniline ($C_6H_5NH_2$) as Brønsted bases and aluminium trichloride ($AlCl_3$) as Lewis acids to produce functionalized silica (In scheme 1 below). The ionically grafted materials obtained from the heterogenization of the Co(II) complexes were systematically characterized by FT-IR spectroscopic methods, thermogravimetry-differential thermal analysis (TG-DTA), optic microscope and SEM are used to determine surface texture and AAS to identification leaching grade (loss of center atom to the solvent). UV-Vis spectrophotometer was also used to determine electronic absorption of the complexes. Moreover, stability of the complexes will be study on the next section.



Scheme 1. The steps to produce functionalized silica. One of the purpose these step is avoid covalently interaction between catalyst and support materials, since its make substrat difficult to attack active sites of catalyst

$$>Si\text{-}OH \; + \; PhNH_2 \longrightarrow \; >Si\text{-}O]\,[H_3NPh]$$

$$>Si\text{-}O]\,[H_3NPh] \xrightarrow{AlCl_3} \; >Si\text{-}O\text{-}\,AlCl_3]\;[H_3NPh]$$

$$>Si\text{-}O\text{-}\,AlCl_3]\;[H_3NPh] + CoCl_2 \xrightarrow{CH_3CN} \; >Si\text{-}O\text{-}\,AlCl_3]_2\,[Co(NCCH_3)_6]$$

$$+\,[PhNH_3]_2\,[Cl_2]$$

Scheme 2. General steps to immobilization homogeneous catalyst. First step which is functionalized surface of silica by introducing Brønsted bases and Lewis acids (scheme 1). Then, by adding Co(II)-acetonitrile complexes as a homogeneous catalyst to functionalized silica would produce immobilized catalyst on modified silica

EXPERIMENTAL SECTION

Materials

The following materials, silica gel (SiO_2), aniline ($C_6H_5NH_2$), aluminium trichloride ($AlCl_3$), cobalt(II) chloride hexahydrate ($CoCl_2.6H_2O$), acetonitrile (CH_3CN), toluene ($C_6H_5CH_3$) and aquadest are used without purification for the synthesis of the functionalized silica and grafting catalyst.

Instrumentation

The obtained catalyst was characterized by FTIR. Cobalt metal loading on modified silica was measured by AAS. Then, electronic absorption of the complexes was measured by UV-Vis spectrophotometer. TG-DTA was used to determine the stability of the immobilat, then, SEM and optic microscopy were used to determine morphology of catalyst surface.

Procedure

Synthetic procedure of support silica

Silica gel was heated at 200°C to form activated silica. Activated silica was mixed with aniline (>Si-OH : N = 1 : 1,2 molar ratio) in 50 mL toluene. Suspension is strirred for 24 hours at room temperature. Then, solution aluminium trichloride is slowly added with a >Si-OH / Al (molar) ratio is 1 : 1,2 by continuing stirring for 24 hours at room temperature. The obtained solid product is filtered and washed repeatedly. The product is modification of silica that called SiO_2-$[AlCl_3]$.

Synthetic procedure of support silica

Indirect method. 1,2 mol $CoCl_2$ anhydrate as starting material is added 30 mL acetonitrile and stirred for 24 hours at room temperature. The obtained mixture solution is analyzed by FT-IR and UV-Vis spectrophotometry method, and the other matter is added support functionalized silica with >Si-OH / Co (molar) ratio is 1 : 1,2 . Then, suspension is stirred for 24 hours at room temperature. The obtained solid product is filtered and washed repeatedly. Solid phase of the grafted catalyst is called SiO_2-[$AlCl_3$]-Co-acetonitrile, and liquid phase is prepared to leaching test.

Direct method. 1,2 mol $CoCl_2$ anhydrate, 30 mL acetonitrile, and modification of silica are stirred together in a batch for 24 hours at room temperature. Then, suspension is formed and obtained solid product is filtered and washed repeatedly. Solid phase of the grafted catalyst is called SiO_2-[$AlCl_3$]-Co-acetonitrile, and liquid phase is prepared to leaching test.

Characterization of Grafted Catalyst

Atomic absorption spectroscopy (AAS) is used to determine the metal loading of the catalyst, UV-Vis spectrophotometry is used to determine the absorption of the complexes. Interactions between silanol group and $AlCl_3$ were identified by fourier transform-infra red spectrophotometry (FT-IR). Thermal stability of the grafted catalyst analyzed by thermogravimetry-differential thermal analysis (TG-DTA) and morphology of the surface was measured by optic microscope and scanning electron microscope (SEM).

Leaching Test

1 g of the solid catalyst SiO_2-[$AlCl_3$]-Co-acetonitrile in acetonitrile and stirred for 24 h. Afterward, the solution part was separated by filtration and analyzed by AAS (Atomic Absorption Spectrophotometer) to determine its Co content.

RESULTS AND DISCUSSION

Silanol group has play important to determining adsorption capacity of the grafted catalysts. Its depend on amount of >Si-OH group per surface area (α_{OH}) which can be calculated theoretically as temperature function [12].

Figure 1 shows the FT-IR spectra of the each compounds. The adsorbtion band at modification of silica shows broadening at 3444,24 cm^{-1} is attributed to streching vibrations of the silanol (Si-OH). The band around 1627,63 cm^{-1} is assigned to a vibration mode of the H-O-H bending [10]. A new weak band around 1493,6 cm^{-1} can be assigned to nitrile (CN) streching aromatic from aniline, when compared with pure silica is not present in the spectra (Figure 1.b). It is one of the evidence Bronsted bases have participated to activated silica surface. Futhermore, the band at 744,388 cm^{-1} is indicated vibration $-NH_2$ wagging from aniline. On the other side, a new weak band at 2800-2900 cm^{-1} is assumed streching mode of the C-H from CH_3CN. The band at 1105,98 cm^{-1} and 799,35 cm^{-1} are attributed to streching vibration of the mesoporous framework siloxane (Si-O-Si) [7,8,10].

Two peak with weak intensity (Figure 1.d and 1.e) at 2350 cm^{-1} is assumed vibration mode of the CN from CH_3CN. Present the two peak with low intensity at this area, indicated the octahedral complexe is formed. The pass away of the shape peaks at 1200-1400 cm^{-1} and 744,388 cm^{-1} of the $C_6H_5NH_3^+$ ion is assumed ion exchange when washed is doing.

UV-Vis spectrophotometry method is used to know the absorbtion of the complexes, not only Co-acetonitrile as a complexe catalyst but Co-water complexe as a standard. Blue complexe is formed from Co-acetonitrile complexe and its seem sharpe peak at 681 nm when analized by UV-Vis spectrophotometry.

Electronic absorbtion is determined both of the complexes (Co-acetonitrile and Co-water complexes). The absorbtion value is comparised to Co-water complexe as the standard. Shifted to higher energy level of the complexe (681 nm to 494,5 nm) is attributed the water molecules as ligands has the ability to remove the acetonitrile which have been coordinated to the center atoms of the complexe. These signed ligand field of the water molecules is more strong than acetonitrile as ligands.

These shifting is occur by splitting of the crystal field between t_{2g} and e_g of the $[Co(NCCH_3)_6]^{+2}$ is small. The effect is the energy that needed to excited of the electrons from t_{2g} to e_g is slightly too. The little energy that needed to excited the electrons that result higher wavelenght, respectively. More small the distance of the energy orbital is assumed the weak ligands, in this case is acetonitrile.

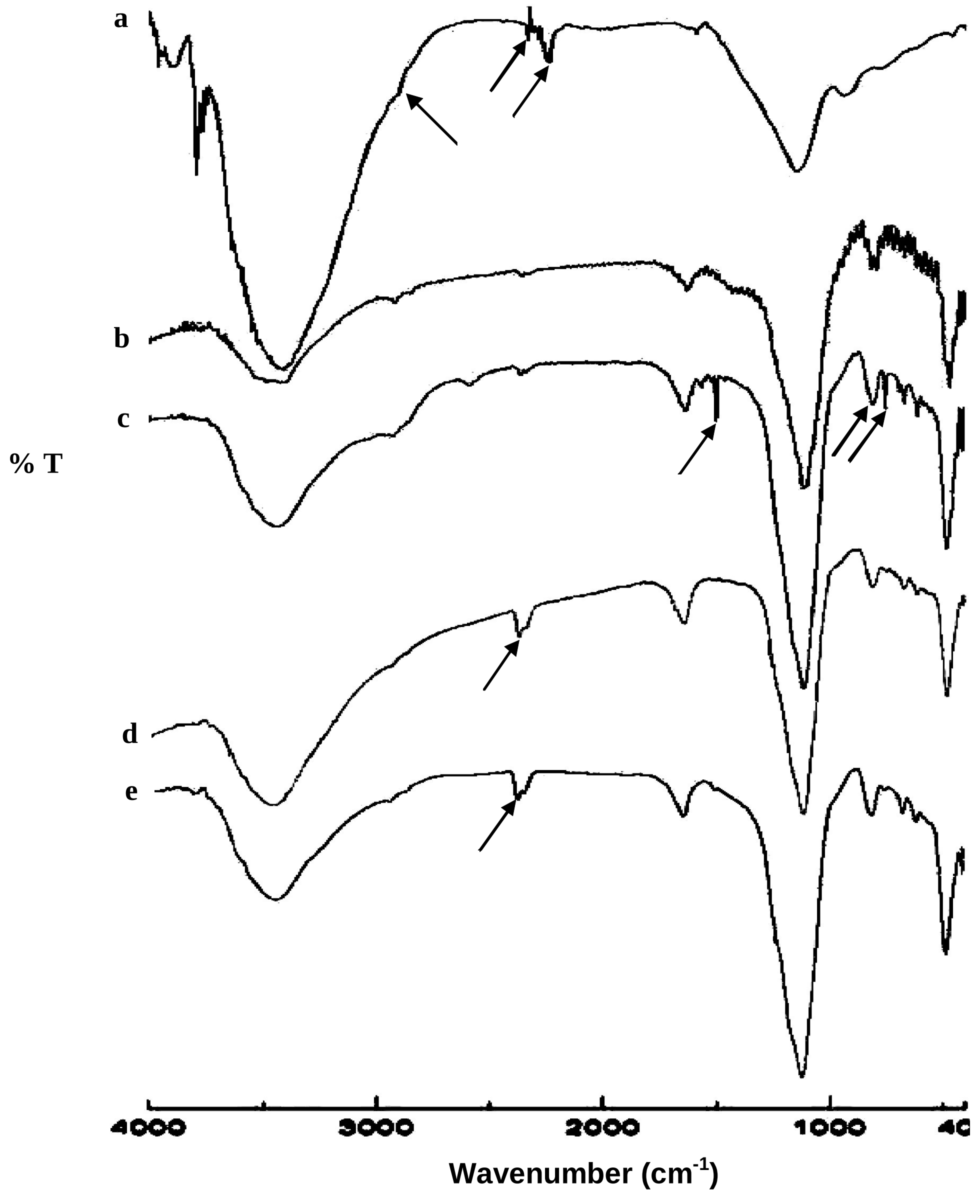


Figure 1. FT-IR spectra of Co-acetonitrile complexe (a), pure silica (b), modification of silica (c), direct immobilat (d) and indirect immobilat (e)

TG-DTA was excecuted for all immobilat. The direct immobilat shows its first decomposition onset at 65,3°C and 661,2°C, being associated with a mass loss of 5,25 % wt. This mass loss is likely to correspond with the loss of the acetonitrile ligands and the anions of the complexes.

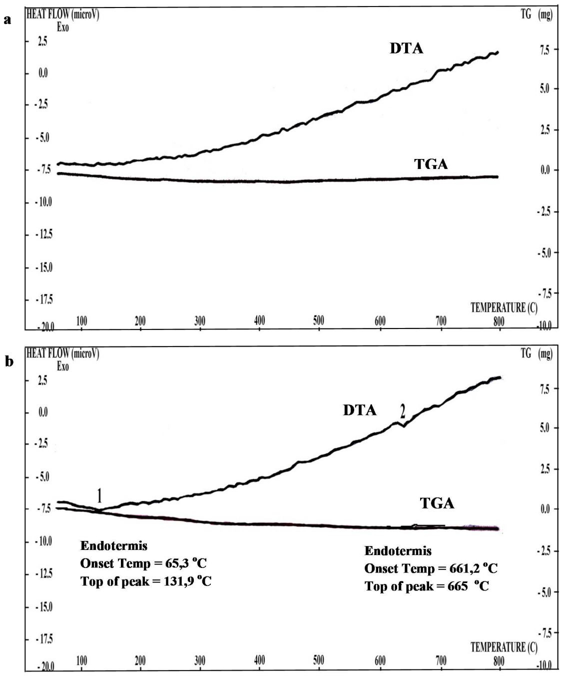


Figure 3. TG-DTA of the direct immobilat (a) and indirect immobilat (b)

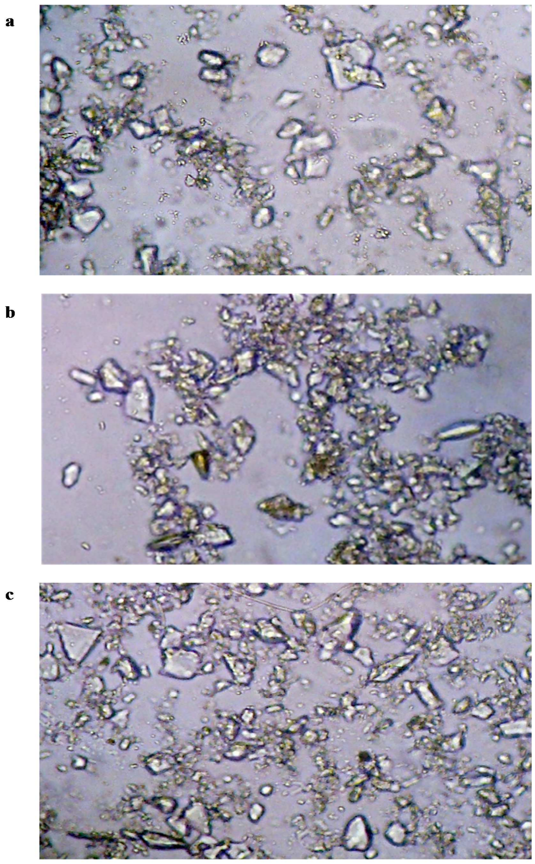


Figure 4. Optic Microscope of the modified silica (a), direct immobilat (b) and indirect immobilat (c) (400 x)

Morphologi of the surfaces can be shown by optic microscope but it not give the more information. When comparised between immobilat and modified silica surface, its have been shown at **b** and **c** of the surface is coated by the catalyst, its attributed the grafting process have been success. To make more evidence SEM images is used to the silica and immobilat.

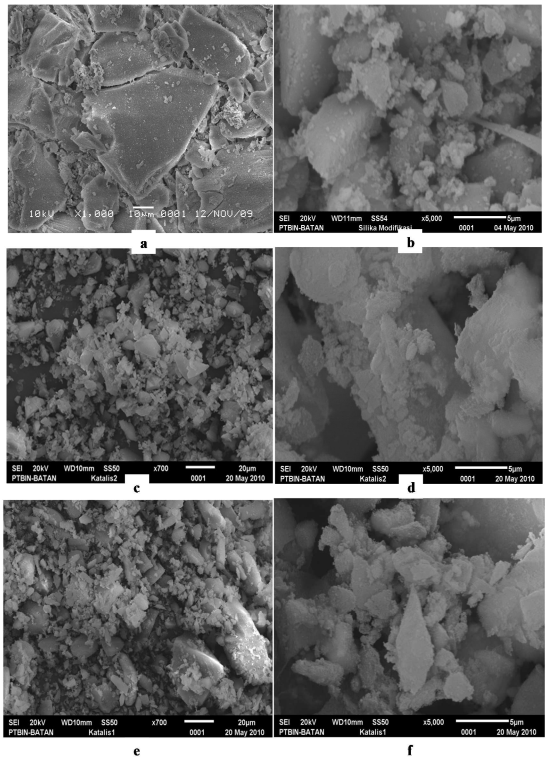


Figure 5. SEM images of pure silica (a), modified silica (b), direct immobilat (c) with 700 x, and (d) 5000 x; indirect immobilat (e) with 700 x, and (f) 5000 x

The SEM images of the grafted samples are providing one of the strong evidence that the grafting method have been success. Its seem that change of the morphologi, indicated the immobilization of the complexe to the silica surface is done. On the other hand, distribution of the complexe at the surface is uniformly. This is indication that immobilization of the catalyst on the modified silica surface have been success.

Direct immobilat has the higher metal loading is 4,576 %. This value is confirmed the cobalt, Co just little binding to the support. On the other side, the loss of weight before and after stability test is signed the higher stability of the immobilat. Metal loading both of the immobilat is not different significanlty. Then, the lower leaching value is direct immobilat at 0,197 %. The most important information from this data is both of the immobilat has the higher stability since the leaching grade is lower.

Table 1. Metal loading and leaching of the samples.

Immobilat	Before stability test (%w/t)	After stability test (%w/t)	Leaching(%)
Direct	4.576	4.567	0.197
Indirect	4.210	4.20	0.237

CONCLUSION

$Co(NCCH_3)_6]^{+2}$ complex is successfully grafted on modified silica surface. Aniline as Bronsted bases and aluminium trichloride as Lewis acids are used to produce modified silica, that make ionic interaction. In general, either direct or indirect grafting produced grafted material with small different. Thermal stability of such complex grafted on the modified silica was moderately high and can be applied until 130°C, and more better if employed in a water free system.

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