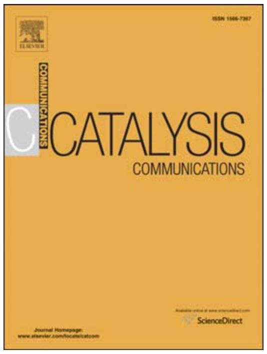

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Molybdenum carbonyl grafted onto silicate intercalated cobalt-aluminum hydrotalcite: A new potential catalyst for the hydroformylation of octene

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Abstract

We present the first example of molybdenum carbonyl grafted on diaminosiloxane-functionalized cobalt-aluminum hydrotalcite (CA-HTSi-DA-Mo) as a promising catalyst for the hydroformylation of olefins. The catalyst showed 80 % conversion with selective formation of branched aldehyde. About 70 % of the catalytic activity retains even after three cycles.

Keywords: Molybdenum carbonyl, Hydroformylation, Hydrotalcite, Olefin

1. **Introduction**

Molybdenum hexacarbonyl ($Mo(CO)_6$) has shown as potential catalyst in various processes such as olefin metathesis [1,2], olefin hydrogenation [3], ketone hydrosilylation and hydrogenation [4,5]. Furthermore, molybdenum carbonyl complexes used as precursors to get molybdenum (VI) oxo catalysts, which have been reported to be efficient agents for the epoxidation of olefins, and have been extensively studied [6-14]. Importantly, $Mo(CO)_6$ has the ability to exchange one or more CO ligands with other donor ligands. The dehydroxylated environment zero-valent Mo in $Mo(CO)_6$ provides active sites for hydrogenation; thus, it is used as a catalyst for hydrogenation and hydrosilyation reactions [15-16]. Mo species in zero-valent and higher oxidation states have a high affinity for olefin groups and are thus able to catalyze hydrogenation, hydrosilylation, oxidation, and metathesis processes. Larhed et al. used $Mo(CO)_6$ as source of CO for carbonylation in the presence of palladium catalysts [17-18]. Furthermore, it has been shown that hetero-bimetallic H-bonded Rh-Mo complexes show cooperative activity in the hydroformylation of cycopentene [19].

Hydroformylation is an important industrial process for the production of aldehydes from alkenes [20], and is generally carried out industrially using a cobalt tetracarbonylhydride $[HCo(CO)_4]$-based catalyst [21-23], or with rhodium-based catalysts [24]. However, cobalt-based catalysts are limited owing to the high *syn*-gas pressure required in their use; rhodium-based catalysts are relatively expensive.

Thus, the development of alternative catalyst that requires less extreme conditions and is less expensive with attractive prospect [19]. $Mo(CO)_6$ possesses good thermal stability and shows excellent catalytic activity and selectivity for hydroformylation when it is combined with other metal carbonyl species [25]. Furthermore, heterogeneous and supported catalysts show improved activity in Fischer-Tropsch (FT) and oxo processes with better catalyst life and selectivity. Consequently, numerous support materials have been utilized for the immobilization of homogeneous catalysts, and their application in hydroformylation has been studied. Among these various supports, hydrotalcites have gained substantial attention owing to their excellent anion-exchange properties and controllable textural features, allowing the intercalation of various organometallic complexes into the interlayer. Hydrotalcite have been shown as promising catalytic supports for several organic reactions [26-32]. It is speculated that the introduction of ($Mo(CO)_6$) into a silicate intercalated cobalt aluminum hydrotalcite (CA-HTSi) support could result in an active species of Mo in the zero-valent state, and the cobalt species present in the HT framework might generate a new class of heterogeneous cooperative catalysis for the olefin hydroformylation. To the best of our knowledge, the utilization of $Mo(CO)_6$ alone as a catalyst for the hydroformylation of olefin, either in homogeneous or supported forms, has not been reported.

The object of the present work is to gain insight into the use of HT-supported molybdenum carbonyl catalysts in the hydroformylation of olefins. We report the first example of $Mo(CO)_6$ incorporation into a diaminosilane-functionalized CA-HTSi support and shown as promising catalyst for the hydroformylation of olefins.

2. **Experimental Section**

2.1. *Preparation protocol*

All the catalyst preparation and grafting procedure were carried out using standard Schlenk techniques under nitrogen atmosphere. Solvents were dried by standard procedures (THF, toluene with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under nitrogen and kept over 4 Å molecular sieves. Silicate intercalated cobalt-aluminum hydrotalcite (CA-HTSi) material was synthesis as per procedure described in literature [30].

The grafting of molybdenum carbonyl was carried out by treating an as-prepared CA-HTSi sample with N-[3-(trimethoxysilyl) propyl]ethylenediamine, followed by reaction with $Mo(CO)_6$ [33]. Different amount of molybdenum carbonyl grafted on silicate intercalated cobalt aluminium hydrotalcite (CoAl-HTSi) was *in-situ* carried out by two-step procedure. First, CoAl-HTSi support (1 g) was pre-activated at 110 ^oC for overnight under vacuum in a Schlenk round bottom flask, then it was cooled to room temperature and introduced calculated amount (4 mmol) of N-[3-(Trimethoxysilyl) propyl] ethylenediamine using dry toluene (30 ml/g support) refluxed for 24 h in nitrogen atmosphere. Then the reaction mixture was cooled down to room temperature and toluene was removed by vacuum filtration. The excess diamine was removed by washing with dichloromethane for several times and the solid was dried using vacuum pump and represented as CA-HTSi-DA. The various quantity such as 1, 2, 3 and 4 mmol of $Mo(CO)_6$ was introduced [33] in toluene / THF on the surface of above prepared CA-HTSi-DA materials to get molybdenum carbonyl grafted materials. The resultant mixture was allowed to stir at 80 ^oC for 4h. The final materials were filter in N_2 atmosphere, washed in dichloromethane and dried in vacuum.

A pictorial representation of the immobilization of $Mo(CO)_6$ on diaminosilane-modified CA-HTSi (CA-HTSi-DA) is shown in Scheme **1**. The samples obtained from the reactions of 1, 2, 3, and 4 mmol of $Mo(CO)_6$ with 1 g of support are represented as CA-HTSi-DA-1Mo, CA-HTSi-DA-2Mo, CA-HTSi-DA-3Mo, and CA-HTSi-DA-4Mo, respectively.

2.2. *Characterization*

Powder XRD was performed to determine the bulk crystalline phases of the materials using a 8 KW XRD Rigaku, Japan with Cu-Kα radiation (λ = 1.54184 Å). The diffraction patterns were recorded in the 2θ range 3-15 and 5–70°, with a scan speed and step size of 0.5°/min and 0.02°, respectively. FT-IR spectra were obtained in the range the range 400–4000 cm^{-1} using KBr pellets (BRUKER, TENSOR 27 FT-IR Spectrometer). The textural properties (BET surface area, micropore area (*t*-plot method), BJH average pore volume) of the samples were derived from N_2 adsorption–desorption measurements carried out at −196 °C out using an automatic micropore physisorption analyzer (Micrometrics ASAP 2020, USA) after the samples were degassed at 110 °C for at least 8 h under 10^{-3}Torr pressure prior to each run. The solid-state NMR experiment was carried out on a Bruker AVANCE 400 narrow bore magnet spectrometer equipped with a superconducting magnet with a field of 9.4 T using a 4 mm double resonance cross-polarized magic angle spinning (CP-MAS) probe operating at resonating frequencies of 79.4 MHz. The sample was packed in 4 mm zirconia rotors and subjected to a spinning speed of 5kHz: single pulse experiment with pulse duration of 4 μs and a relaxation delay time of 5 s were used with 2000 number of scans. The chemical shift values are expressed with respect to TMS. Thermogravimetry-analysis (TGA) was carried out in a Thermal Analyzer (Model-2950, TA Instruments, and USA). About 5–10 mg of the sample was taken in the platinum pan and heated in air at the heating rate of 10 ^{o}C min $^{-1}$ up to 800 ^{o}C. The amount of molybdenum content in the sample was determined by inductively coupled plasma – atomic emission spectroscopy (ICP – AES; Model: Optima 8300, Make: Perkin Elmer). The sample was obtained by digesting CA-HTSi-DA-Mo materials with equal volume (6 ml) mixture containing H_2O_2, ammonium hydroxide and ethanol. The resultant mixture was filter by whatman filter paper and the filtrate was made into 100 ml. The solution was aspirated into plasma of ICP-AES equipment and concentration of Mo in the samples was obtained with respect to standard solution of Mo (Emerck, Germany).

2.3. *Catalytic study*

The hydroformylation reactions were performed in 100 ml stainless steel autoclave (Amar Equipment India Pvt. Ltd). In a typical experiment, required amount of catalyst (0.15 gm), 1-octene

(0.0191 M; 3 ml) and solvent (3 ml) were charged into the reactor under nitrogen atmosphere and the stirrer was adjusted to (250) rpm. The reactor was purged with CO and H_2 (1:1) mixture with desired pressure and the temperature reached to preferred temperature with constant stirring. After the reaction completion, the stirrer was stopped, reactor was cooled to room temperature with water circulation, depressurized and the product was collected and were analyzed using gas chromatography equipped with FID (Agilent 7890A Series) connected to a HP-5 capillary column (30 m; HP-5). Further, the different products such as isomerized, hydrogenated and hydroformylated (Scheme **2**) were confirmed using GC-MS (Agilent). Conversion of 1-octene and also the selectivity of the products were calculated based on the following formula

$$\text{Conversion of 1-octene} = \frac{O_i + O_H + O_{CHO} + O_{OH}}{O_1 + O_i + O_H + O_{CHO} + O_{OH}}$$

$$\text{Selectivity of aldehyde products} = \frac{O_{CHO}}{O_i + O_H + O_{CHO} + O_{OH}}$$

Where O_1, O_i, O_H, O_{CHO}, and O_{OH} are mole of unreacted 1-octene, octene isomers (excluding 1-octene), hydrogenated octene, hydroformylated octene and alcohol in the products respectively.

3. **Results and Discussion**

Powder XRD patterns of pure CA-HTSi and the $Mo(CO)_6$ grafted samples viz., CA-HTSi-DA-1Mo and CA-HTSi-DA-3Mo are shown in Fig. 1. All the samples exhibit broad reflections around 2θ of 10°–16° and 25°–32°, characteristic of the (003) and (006) planes of an HT-layered structure [26-32]. The parent CoAl-HT shows an additional peak (Fig. 1a) which is characteristic of (0 0 1) plane and it disappeared upon the introduction of bulk diammine functional group and $Mo(CO)_6$, owing to filling of guest molecules in the interlayer space. The presence of diaminosilane and $Mo(CO)_6$ between the interlayer of CoAl-HT clearly evident from decrease in unit cell parameter along “c” axis

(Table 1). Further, the broadening of the XRD reflections in the molybdenum-grafted samples is due to the orientation of the interlayer species and the presence of siloxane functionality on the external surface of the layered HT [26-32]. The absence of any XRD reflection corresponding to $Mo(CO)_6$ even under maximum loading indicates the uniform distribution of grafted active molybdenum species onto the diamino functionality present on the surface of hydrotalcite. The broadening of the XRD reflection may also be due to the decrease in the particle sizes of the support owing to the presence of a bulk silicate host on the interlayer [29-32].

FT-IR spectra of CA-HTSi, and molybdenum carbonyl grafted samples are depicted in Fig. 2. All samples showed vibrational bands around 1081 and 800 cm^{-1} due to asymmetric and symmetric vibrations of interlayer silicate species. Absence of band around 1370 cm^{-1} corresponds carbonate ion for the CA-HTSi-DA-Mo samples clearly evidence that the interlayer are completely filled with silicate anions and silane linker which in turn connected on this interlayer silicate [29-31]. A shoulder peak appearing at approximately 2850 cm^{-1}in the spectrum of the CA-HTSi-DA sample is due to the ethane (C_2H_4) functionality present between (NH) groups. The CA-HTSi-DA-Mo samples showed a new weak broad band around 2010, 1986, and 1930 cm^{-1} respectively, which can be assigned to the (CO) group vibrations of the in situ grafted molybdenum carbonyl species on the surface of CA-HTSi-DA [6,11,12]. The relative intensity of the above vibrational band increases with increase in molybdenum carbonyl loading.

In order to confirm the heterogenization of molybdenum carbonyl on CA-HTSi, ^{29}SiMAS-NMR analysis was performed on CA-HTSi-DA-3Mo, and the result is displayed in Fig. 3. CA-HTSi-DA-3Mo showed resonance peaks at -101.6, -90.8, and -82 ppm, corresponding to the presence of silicon in different environments on the hydrotalcite framework, such as Q_3, Q_2, and Q_1 sites, respectively [$Q_n = Si(OSi)_n(OM)_{4-n}$, where M = H, Al, or Co]. The additional broad shoulder peaks evident around the region varying from -45 to -25 ppm correspond to organosilica species, which come from N-[3-(trimethoxysilyl) propyl]ethylenediamine ligands connected to the surface silica species present on the interlayer of HT. The textural properties of CA-HTSi and the $Mo(CO)_6$-grafted samples are summarized in Table 1. The BET surface areas of ligand-modified hydrotalcite and $Mo(CO)_6$-grafted samples are found to be lesser than the parent cobalt-aluminum hydrotalcite. The grafting of molybdenum carbonyl through the diamine linker on the HT surface results in decreases the surface area and pore volume [11, 12]. However, the interparticle pore size remains intact, indicating that the support is stable even after high loading with $Mo(CO)_6$. The estimated molybdenum content in various CA-HTSi-DA-Mo samples by ICP-AES analysis is shown in Table 1. It is clear from the table that all the samples shows similar Mo content to that of theoretical value indicates the molybdenum species effectively anchored on the surface of diammine.

Hydroformylation of 1-octene using CA-HTSi-DA-Mo materials were systematically evaluated in the liquid phase medium and the results are summarized in Table 2. The pure support CA-HTSi showed about 40 % conversion. Though, the hydroformylated product had poor selectivity because the olefin undergoes polymerization on the support surface. The introduction of diamine functionality on the CoAlHT materials inhibits the hydroformylation, however, it favored the formation of olefin isomerized product alone. On the other hand, the introduction of $Mo(CO)_6$ moiety at lower concentration (1mmol per gram of support) improves the octene conversion. The selectivity of aldehyde was poor and a considerable amount of hydrogenated side-product was also observed. This could be due to the presence of isolated molybdenum species on the catalyst has the ability to abstract hydrogen and favour the formation of considerable amount of hydrogenated product [34-35]. Upon increasing of the $Mo(CO)_6$ loading increase in conversion of octene and reaches the maximum of about 87–90%. The concentration of $Mo(CO)_6$ loading in the range of 3–4 mmol per gram of support favors the maximum selectivity of hydroformylated products. The increase in loading of Mo(CO)$_6$ on the support favors the presence of active Mo species in the vicinity of divalent cobalt ions present in the layer HT, which cooperatively help on enhance the selectivity of hydroformylation products (see Scheme **3**).

Importantly pure Mo(CO)$_6$ doesn't show any hydroformylation activity. Thus it supports the co-operative mechanism between cobalt species present in hydrotalcite framework and molybdenum carbonyl present on the surface diammine, which may lead to the formation of the hydroformylated product with 75–80 % of selectivity and about 8–9 % of alcohol side-product which appeared in all cases. Linear aldehyde was obtained in about 20 % selectivity and the major products were identified as branched aldehydes. In order to understand the co-operative mechanism, the reaction was studied using physical mixture of CoAl-HT and Mo(CO)$_6$, which doesn't show any hydroformylated product, rather it yield olefin isomerized and hydrogenated products. The presence of surface hydroxyl group on CoAl-HT destabilize Mo(CO)$_6$ and favored the formation of olefin isomerized and hydrogenated products [34-35] by hydrogen abstraction.

Inorder to improve the hydroformylation product, the reaction was studied by varying the catalyst amount (CoAl-HT-DA-3Mo) and the results are provided in Table 3. The increase in catalyst loading increases the 1-octene conversion with the formation of exclusive hydroformylated products. However, the product distribution of linear and branched aldehyde remains constant. The effect of reaction time on 1-octene conversion, hydroformylated product selectivity and aldehyde distribution over CoAl-HT-DA-3Mo are shown in Figure 4. In initial hours considerable amounts of olefin isomerized products were formed. However, 1-octene conversion and hydroformylated products increased steadily with increase in reaction time and reaches maximum around 7-8 h (Fig. 4 a). Although the formation of linear aldehyde is predominant at initial hour, the branched aldehyde selectivity increases with the course of time (Fig. 4b). The decrease in pressure and temperature also results in drastic decrease in hydroformylation of 1-octene were evident (Table 3).

The recyclability of the catalysts was studied under optimized conditions (T = 200 ^{o}C, P = 90 bar, 1-octene (3 ml), CoAl-HT-DA-3Mo = 0.15 gm, t = 8 h), and the results are summarized in Table 4. It is clear from the table that catalytic activity decreases drastically and reaches a minimum conversion of about 16 % with the aldehyde selectivity of 6 %, after four cycles, which is due to the conversion of molybdenum carbonyl species into oxo species when exposed to the atmosphere during the recycle process. In order to preserve the active sites, attempts were made using dry toluene as solvent, and a similar initial activity was observed. Importantly, the catalytic activity was about 77 % preserved even after four cycles (see Table 4) with selective formation of hydroformylated products. The observed decrease in the catalytic activity is due to the adsorption of reactant / product molecules on active sites of the catalysts during the reaction. This is supported from TG-DTA analysis of spent catalyst (Fig. 5), which showed about 35 % weight loss derived from decomposition of diammine functional group and chemisorbed organics present on the surface. In addition N_2 sorption analysis of used catalyst (Table 1) further supports the above fact, where a drastic decrease in surface area and pore volume occurred owing to accumulated organic, which accounts the observed decrease in conversion on recycle catalyst.

Conclusion

The current study reveals that the $Mo(CO)_6$ supported catalyst can be prospective alternative hydroformylation catalyst when it is supported on cobalt based hydrotalcite materials. To the best of our knowledge, this is the first report of a $Mo(CO)_6$ based supported catalyst for the hydroformylation of an olefin. Further details on mechanistic aspects and their importance for various olefins is the subject of interest will be explored.

Authors contributions

¥Authors Nihar Ranjan Mahato and Thangaraj Baskaran, contributed equally.

Acknowledgments

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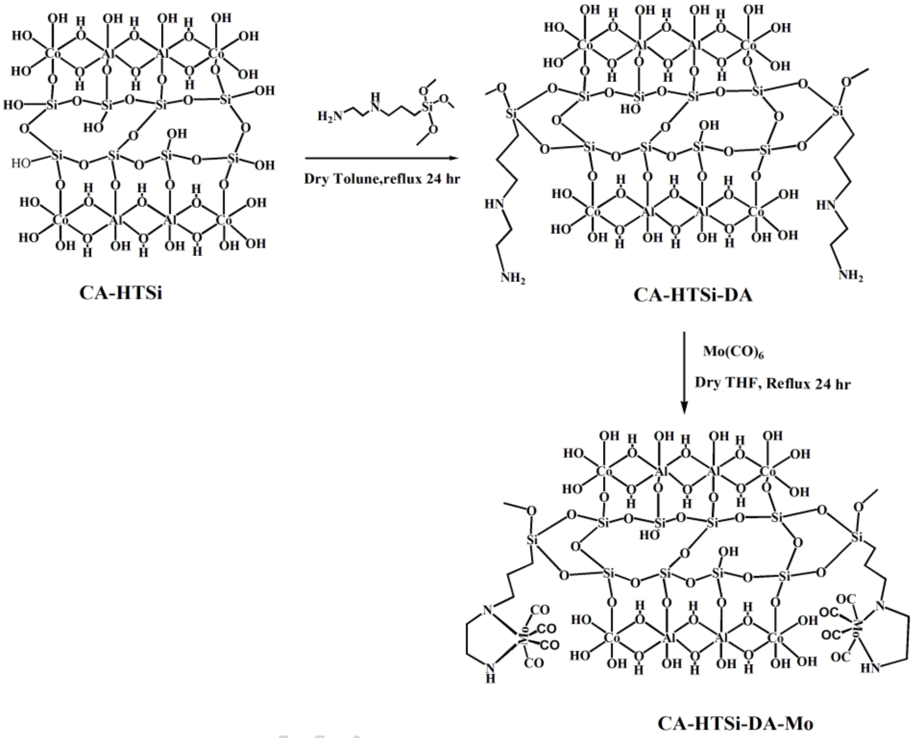
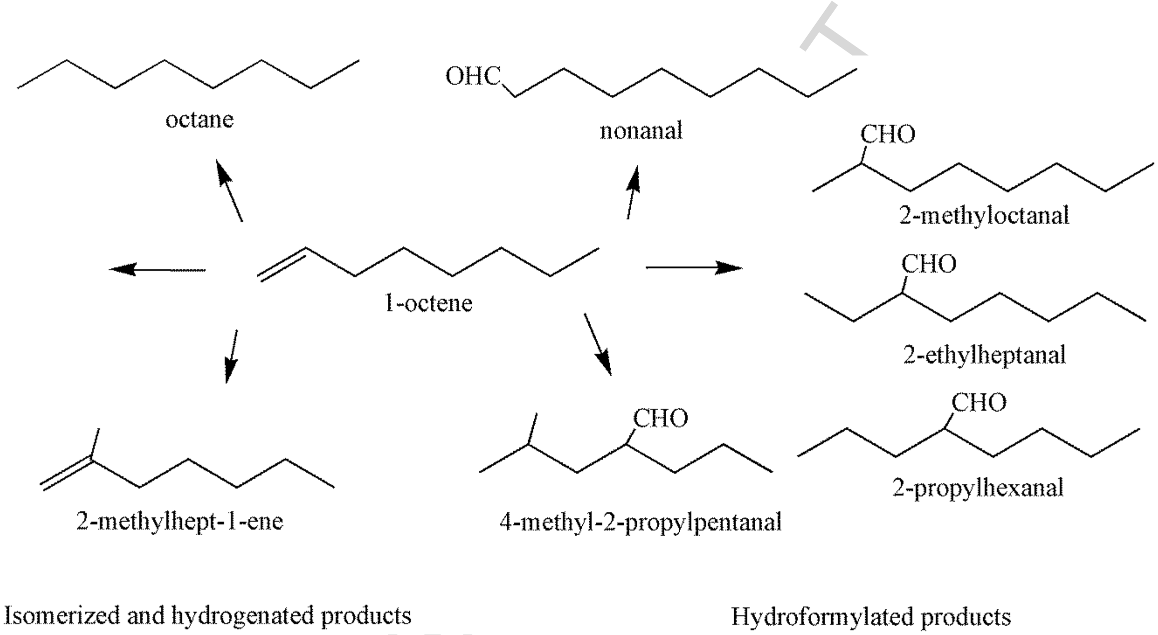
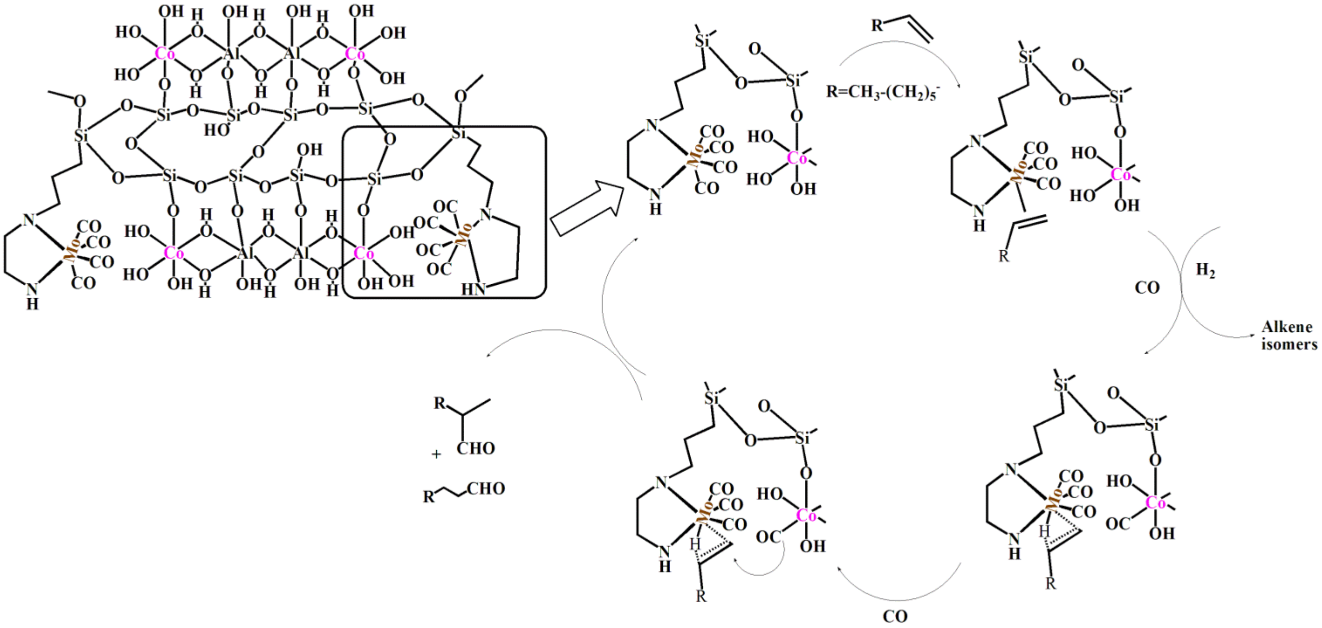


Scheme **1**. Pictorial representation of $Mo(CO)_6$ grafted on diaminosiloxane-functionalized hydrotalcite (CA-HTSi-DA).



Scheme **2**. Schematic representation of various products derived on CA-HTSi-DA-Mo catalysts.



Scheme **3**. Schematic representation of various products derived on CA-HTSi-DA-Mo catalysts.

Figure Caption

Fig. 1. XRD patterns of CA-HTSi and molybdenum carbonyl grafted CA-HTSi materials (a) Lower and (b) Wider angle pattern.

Fig. 2. FT-IR spectra of (a) CA-HTSi, (b) CA-HTSi-DA-1Mo, (c) CA-HTSi-DA-3Mo and (d) CA-HTSi-DA-3Mo recycled.

Fig. 3.^{29}SiMAS-NMR spectrum of CA-HTSi-DA-3Mo.

Fig. 4. Effect of reaction time on (a) 1-octene conversion and product selectivies on CA-HTSi-DA-3Mo and (b) distribution of aldehyde on CA-HTSi-DA-3Mo

Fig. 5. TGA profile of (a) recycled CA-HTSi-DA-3Mo and (b) DTA profile of recycled CA-HTSi-DA-3Mo.

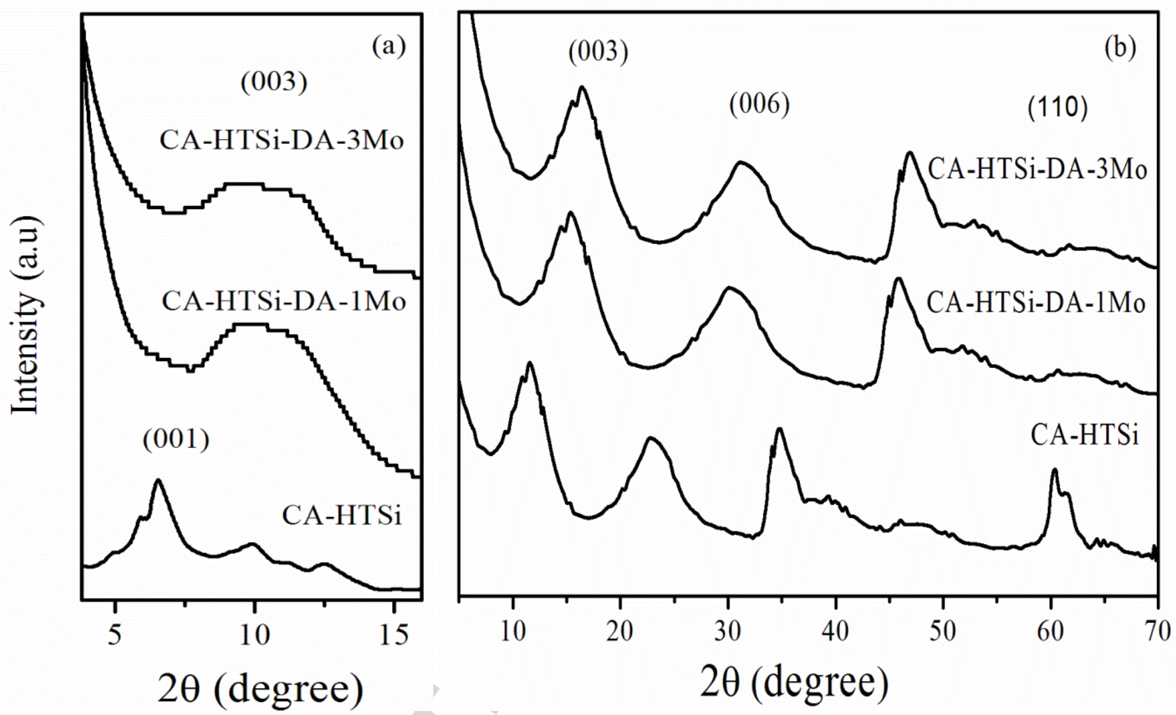


Fig. 1.Sakthivel et al.

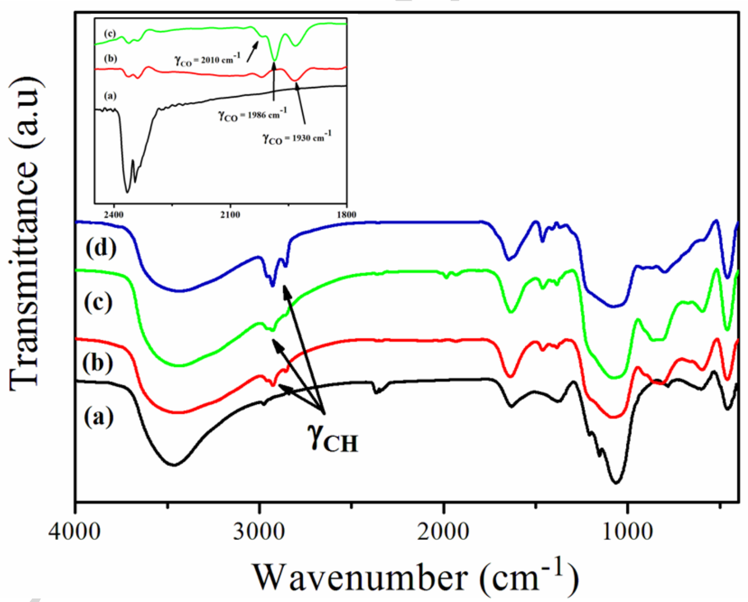


Fig. 2.Sakthivel et al.

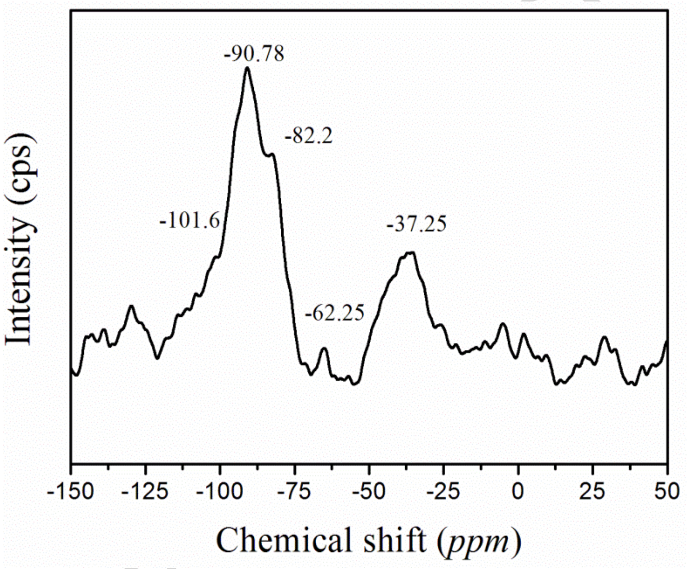


Fig. 3. Sakthivel et al.

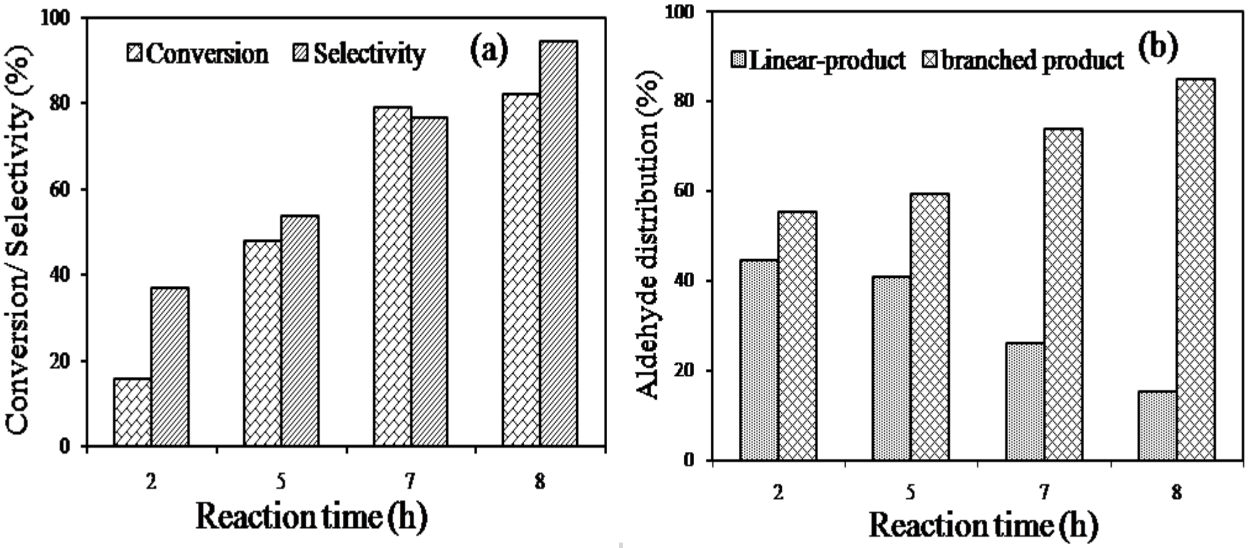


Fig. 4. Sakthivel et al.

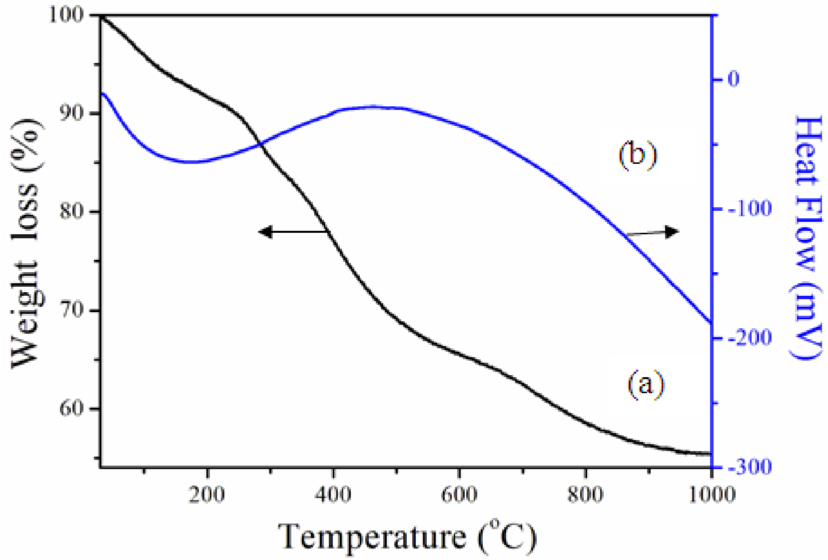


Fig. 5.Sakthivel et al.

Table 1. Textural properties of CA-HTSi and CA-HTSi-DA-Mo materials.

S. No.	Sample details	BET Surface area (m^2g^{-1})	Pore volume ($cm^3\ g^{-1}$)	Inter particules size (nm)	Mo content (wt. %)[‡]	Unit Cell parametres (A°)	
						a	c
1	CA-HTSi	332.1	1.23	13.3	--	2.50	24.3
2	CA-HTSi-DA	210.7	0.95	13.8	--	--	--
3	CA-HTSi-DA-1Mo	213.4	0.80	13.7	8	2.48	17.8
4	CA-HTSi-DA-2Mo	162.2	0.70	13.6	--	2.48	17.0
5	CA-HTSi-DA-3Mo	166.7	0.66	13.2	28	2.47	16.3
6	CA-HTSi-DA-3Mo-recycled	17.3	0.07	10.3	27	--	--
7	CA-HTSi-DA-4Mo	205.2	0.73	12.3	32	--	--

[‡] Calcuated based on ICP-AES analysis

Table 2. Hydroformylation of 1-octene on CA-HTSi-DA-Mo catalysts.

Catalysts	Conv. (%)	Selectivity of products (%)[‡]			Distribution of aldehyde (%)	
		H[#]	CHO[#]	OH[#]	linear	Branched
CA-HTSi	40.0	5.7	32	0.0	33.6	67.4
CA-HTSi-DA	0.5	0.5	0.0	0.0	00.0	00.0
CA-HTSi-DA-1Mo	51.0	20	9.7	21.3	03.5	96.5
CA-HTSi-DA-2Mo	82.0	2.3	71	8.7	22.5	77.5
CA-HTSi-DA-3Mo	87.0	0.0	85	7.5	20.3	79.7
CA-HTSi-DA-4Mo	91.0	0.8	81	9.6	20.5	79.5

[†]Reaction conditions: Temperature = 200 ^{o}C; Pressure = 90 bar, 1-octene: 0.0191mole (3 ml), catalyst: 0.15 gm, time = 8 h. [#]H = Hydrogenated product, [#]CHO = Hydroformylated products, [#]OH = Alcohol products; [‡] Remaining products are 1-octene isomerized products and trace amount of polymer.

Table 3. Effect of catalyst amount and temperature on hydroformylation of 1-octene on CoAl-HT-DA-3Mo.

Catalyst amount (g)	Temperature (^{o}C)	Conv. (%)	Pressure (bar)	Selectivity of products (%)			Distribution of aldehyde (%)	
				H[#]	CHO[#]	OH[#]	linear	Branched
0.15	200	55.4	70	--	100	--	29.7	70.3
0.15	190	24.0	90	--	90.7	9.3	37.0	63.0
0.15	200	82.0	90	--	94.5	4.6	15.2	84.8
0.21	200	89.0	90	--	98.3	1.7	13.0	87.0
0.3	200	91.0	90	--	100	--	15.6	84.4

[†]Reaction conditions: Temperature = 200 ^{o}C; 1-octene: 0.0191mole (3 ml), time = 8 h, Solvent = Toluene (3 ml). [#]H = Hydrogenated product, CHO = Hydroformylated products, OH = Alcohol products.

Table 4. Effect of solvent and recyclability of CA-HTSi-DA-Mo catalysts for Hydroformylation of 1-octene.

Catalysts	Conv. (%)	Selectivity of products (%)[‡]			Distribution of aldehyde (%)	
		H[#]	CHO[#]	OH[#]	linear	Branched
CA-HTSi-DA-3Mo[‡]	87.0	0.0	85.0	7.5	20.3	79.7
2nd cycle[‡]	40.8	2.0	94.0	4.0	24.0	76.0
4th cycle[‡]	16.0	8.7	5.8	1.3	28.9	71.1
CA-HTSi-DA-3Mo[γ]	82.0	--	94.5	4.6	15.2	84.8
2nd cycle[γ]	76.2	--	96.2	3.8	18.7	81.3
4th cycle[γ]	63.2	--	100	0.0	29.7	70.3

[†] Reaction conditions: Temperature = 200 °C; Pressure = 90 bar, 1-octene: 0.0191mole (3 ml), catalyst: 0.15 gm, time = 8 h, [‡] Reaction carried out without solvent. [#] H = Hydrogenated product, CHO = Hydroformylated products, OH = Alcohol products. [γ] Reaction studied in presence of toluene as solvent (3 ml). [‡] Remaining products are 1-octene isomerized products and trace amount of polymer.

Molybdenum carbonyl grafted onto silicate intercalated cobalt-aluminum hydrotalcite: A new potential catalyst for the hydroformylation of octene

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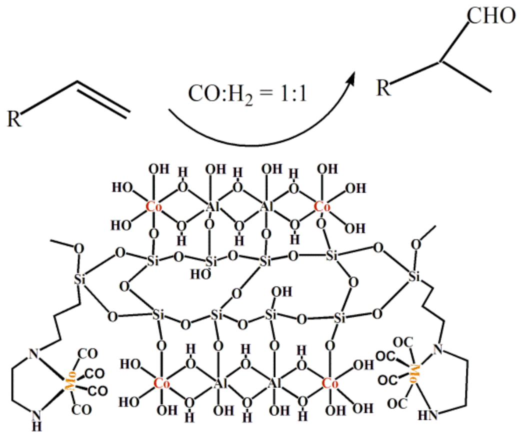
First example of molybdenum carbonyl grafted on cobalt aluminum hydrotalcite (CA-HTSi-DA-Mo) support is shown as promising catalyst for the hydroformylation of olefins.



Graphical abstract

Molybdenum carbonyl grafted onto silicate intercalated cobalt-aluminum hydrotalcite: A new potential catalyst for the hydroformylation of octene

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Highlights

- First example of molybdenum carbonyl based catalyst for hydroformylation.
- Introduction of $Mo(CO)_6$ on CoAl-HT help on cooperative mechanism.
- Heterogenization evident from ^{29}Si MAS-NMR and FT-IR
- Catalyst showed 80 % olefin conversion and branched aldehyde selectivity.