

in-situ generation of surface-active $HCo(CO)_y$ like intermediate from gold supported on ion-promoted Co_3O_4 for induced hydroformylation-hydrogenation of alkenes to alcohols

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in-situ generation of surface-active HCo(CO)_y like intermediate from gold supported on ion-promoted Co₃O₄ for induced hydroformylationhydrogenation of alkenes to alcohols

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Highlights

- Gold nanoparticles supported on alkali ion-promoted mesoporous Co₃O₄ were synthesized and characterized using various instrumental techniques.
- The catalysts were evaluated for the hydroformylation-hydrogenation of 1-octene to nonanol under syngas H_2/CO (2:1) pressure.

• The products of the 1-octene hydroformylation-hydrogenation reaction were analyzed by GC-MS and GC-FID analyses.

Abstract

In this study, a greener and stable surface-active cobalt-carbonyl like specie $[HCo(CO)_y]$ was generated via H₂ and CO spillover by gold on ion-promoted cobalt oxide. The supports and catalysts syntheses were based on inverse micelle and deposition-precipitation methods, respectively. The temperature-programmed reduction was used for optimization to obtain the best supports. The catalysts with activity (Co₃O₄ < Cs-Co₃O₄ < Au/Cs-Co₃O₄ and Au loadings 10% < 2% < 5%) were evaluated for the hydroformylation-hydrogenation of alkenes to alcohols, with the 5% Au/Cs-Co₃O₄ catalyst more active than the others and displayed excellent alcohol chemoselectivity with varying regioselectivity under milder reaction conditions. The reaction was assumed to take place via the formation of $[HCo(CO)_y]$ specie, as the active catalytic site of the catalyst. The enhanced catalytic performance was also ascribed to the low-temperature reducibility and surface basicity of the nanomaterials. The stability of the catalyst was evaluated by recycling, with its mesostructure retained after four cycles.

Keywords: Hydroformylation-Hydrogenation; Mesoporous cobalt; Gold catalyst; Ion-promoters; 1-octene; Alcohol.

1.0 Introduction:

Hydroformylation, also known as oxo reaction, remains a vital process in academic and industrial perspectives for the synthesis of alcohols and aldehydes from alkenes. In 1938, Otto Roelen discovered hydroformylation reaction and patented it in 1943 [1]. Approximately eight (8) million metric tons of alcohols and aldehydes are produced via hydroformylation reactions. These products have found usage in the manufacturing of surfactants, detergents, adhesives, soaps, solvents, and plasticizers. Commercially, phosphine modified rhodium-based catalysts have been widely reported for the hydroformylation of alkenes with shorter chain length (C₂-C₆) under milder reaction conditions. However, this homogeneous catalyst cannot be employed for longer chain alkenes due to the decomposition of the rhodium catalyst during separation from the mixture and for reuse in subsequent reactions [2,3].

Although, homogeneous catalysts give higher conversion and product selectivity in shorter reaction time compared to its heterogeneous counterpart, but with problems of separating the catalyst from

the reaction mixture. On the other hand, cobalt metal is less expensive than rhodium, and its carbonyl-based catalysts ([Co₂(CO)₈] and [Co(CO)₃PR₃]) have been reported for higher alkene hydroformylation under homogeneous conditions. Alternative metals like Pt, Pd, Fe, and Ru have also been reported as hydroformylation catalysts [4]. However, the use of these cobalt carbonyl complexes requires a rather harsh condition of temperature, syngas pressure of >24 MPa, and longer reaction time to stabilize the catalyst. This method often involves recrystallization and sublimation before use to obtain a good product yield and reusability, due to the dissociation of CO during storage below 0 °C and under an inert gas atmosphere [5]. The practical utility in the synthesis of these cobalt carbonyl-based catalysts is still limited to problems of volatility, toxicity, the formation of insoluble carbonyl clusters, and separation of the carbonyls from the reaction mixture [5,6]. One possible solution is to heterogenize this cobalt catalyst by depositing it on supports such as resins [7,8], activated carbon [9], and SiO₂ [10]. Immobilization of active sites on these supports through physical and chemical interactions can form heterogeneous catalysts, which in turn leads to an environmental and economically friendly "green" process chemistry. Given this, developments of heterogeneous catalytic systems are gaining broad research interest in various carbonylative transformations, such as hydroformylation reaction. In recent time, carbonylation reactions involving noble metal nanoparticles are quite useful, efficient, and gives excellent product yields.

Metal nanoparticles are the subject of intense interest in materials science and chemistry because they display unusual chemical and physical properties, which are distinct from those of both isolated molecule and bulk phase [11,12]. Particularly, gold catalysis has led to alternative, competitive strategies and highly innovative discoveries that have laid down a foundation for the implementation of various catalytic transformations. A few decades ago, gold was considered to be chemically inert and catalytically inactive as a catalyst for hydrogenation or oxidation reactions at ambient temperature. To contradict these ideas, Sermon and Bond in 1973 reported that highly dispersed supported gold nanoparticles can chemisorb hydrogen gas at a temperature as low as 120 °C, and can catalyze hydro-cracking and hydrogenation reactions at ambient temperatures [13]. Gold nanoparticles (AuNPs) are well-known for their enhanced catalytic activity in numerous heterogeneous and homogeneous reactions, such cycloaddition [14], C-C coupling [15], hydroamination [16–18], amidocarbonylation [19], oxidative cyclization [20,21], hydroalkoxylation [22], oxidation [23] and reduction [24]. The most important key is to support AuNPs on selected mesoporous metal oxides (MMOs) to afford a bimetallic structure. Although the choice of this support affects the durability and performance of the catalysts, and the supported gold nanoparticles on mesoporous metal oxides can moderately absorb CO gas [25]. Mesoporous metal oxides have

been of intense research interest due to its applications in separation, adsorption, gas storage, electrochemistry, and catalysis [26–28]. These mesoporous materials have tunable pore size diameters within the range of 2 to 50 nm, large surface area, and their crystal structures are the most intrinsic features supporting their numerous applications [29,30].

Several works of literature on heterogeneous gold supported on MMOs have been reported for reactions involving CO gas. Investigation of the oxygen storage capacity of mesoporous titania supported gold catalysts for CO oxidation has been widely reported. Notably, the influence of the nano-sized gold in the CO spillover mechanism [31–35]. Similarly, MMOs supported gold catalyst has been reported for other types of carbonylation reactions, such as amidocarbonylation [19], and cyclocarbonylation [36]. Tokunaga and co-workers reported that hydroformylation reactions could proceed smoothly on supported gold catalysts under the syngas atmosphere. In these reactions, the investigation of the role of AuNPs in providing spillover of carbon monoxide and hydrogen gas was reported [37]. Therefore, heterogeneous supported gold catalysts has proven to be of great alternative to homogeneous metal carbonyls, and are ideal choice, in terms of catalyst separation, easy preparatory steps and reusability.

The applicability of this noble-transition metal catalyst for the hydroformylation-hydrogenation of alkenes to alcohols, to better understand the synergistic effects is limited. Although, few researchers have reported the reductive hydroformylation reaction using a combination of transition metals in the form of Co-Rh [38] and Fe-Cu [39] under homogeneous conditions. Alcohol synthesis via reductive hydroformylation is a vital reaction sequence, which directly converts alkene compounds to alcohols. The use of syngas (H₂/CO), in varying ratios, is more advantageous and eliminates the risk of using hydrogen for aldehyde hydrogenation in a multi-step process. To date, hydroformylation-hydrogenation reactions using modified palladium, cobalt, and ruthenium catalyst have been reported [40]. Recently, a new modified homogeneous cobalt complex with phosphine ligand has been reported for the reductive hydroformylation of higher alkenes to alcohol [41]. Liu and co-workers extensively studied the hydroformylation-hydrogenation of alkenes to alcohol via a reverse water-gas shift [42]. The reductive hydroformylation of alkenes to alcohols using a fibrous cobalt oxide catalyst has also been reported [43], and the reaction proceeded at temperatures ranging from 150-170 °C. Llorca and co-workers reported the alcohol synthesis by hydroformylationhydrogenation of ethene, using a homogeneous cobalt carbonyl cluster [44]. Yang et al. have reported a supported gold catalyst modified with phosphine ligand for the one-pot synthesis of tricyclodecanedimethylol (TDDMO) [45]. The AuNPs assisted in the formation of a phosphine complex, as active catalytic sites on the catalyst. The poor chemo- and regio-selectivity, harsh

reaction conditions, catalyst separation, and cost of the phosphine ligands, were the major limitations associated with this multi-step synthetic protocol. Also, it was impossible to investigate the activity and structural relationship in the mixed catalytic systems. Therefore, on an economic larger scale, higher alkene hydroformylation-hydrogenation processes with these catalytic systems are not applicable. For this reason, the development of an effective, stable and highly reusable heterogeneous catalysts for reactions involving CO, and to better understand their activity-structural relationship is desirable. Hence, heterogeneous catalysts present more advantages to its homogeneous counterparts, in terms of catalyst recovery and reusability.

By putting the advantages of heterogeneous catalytic systems into consideration, and to continue our ongoing research on the use of the gold catalyst in heterogeneous carbonylation reactions, herein, we aim to synthesize mesoporous Co₃O₄ support by dopping with alkali metals (ion-promoters) via inverse micelle approach [46]. Subsequently, the immobilization of gold nanoparticles on the modified support to afford a bimetallic structure. As earlier reported in our group, alkali metals on mesoporous Co₃O₄ tend to improve catalytic activities of various industrial chemical reactions to a great extent [47]. Although several works have reported the enhanced catalytic efficiency of alkalidoped metal oxides [48–50], this is due to the dopant's structural [51] and electronic [49,50] effects on the mesoporous metal oxides. The synergy, parameters effects (catalyst loading, partial pressure, temperature, and time), kinetics, reusability, and catalytic activity in terms of low-temperature reducibility and increase in surface basicity of the catalysts were studied in detail. The supported gold catalyst was applied for the hydroformylation-hydrogenation reaction (Scheme 1) of various alkenes, by investigating the role and effects of the AuNPs and alkali metals on the catalyst.



Scheme 1. 5% Au/Cs-Co₃O₄ catalyzed hydroformylation-hydrogenation of 1-octene.

2.0 Experimental

2.1. Chemicals and reagents

Gold(III) chloride trihydrate (99.9%), potassium tetrachloroplatinate(II) (\geq 99.9%), nitric acid (HNO₃) (70%), cobalt(II) nitrate hexahydrate (98.8%), 1-butanol (\geq 99.8%), tetrahydrofuran (99%), acetonitrile (99%), hexane (99.8%), toluene (99.9%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) Pluronic (P-123), 1-octene (98%), pentene (98%), hexene (98.8%), heptene (98%), styrene (98.8%), nitrate salts of sodium (98%), cesium (98%), lithium (98.8%), sodium borohydride (\geq 96%) and urea (\geq 99.9%) were purchased from Sigma-Aldrich. The nitrate salts of calcium (\geq 98%) and potassium (99%) were purchased from Associated Chemical Enterprises. The synthesis gas H₂/CO (2:1) was purchased from AFROX Chemicals, RSA. Milli-Q water was used in the synthesis of the catalysts. All chemicals were of analytical grades and used without further purification.

2.2. Synthesis of the supports and catalysts

Mesoporous Co₃O₄ at different temperatures (150-550 °C) were prepared via the inverse micelle approach with modification [46]. In a typical synthesis, 5.82 g (20 mmol) of Co(NO₃)₂·6H₂O was dissolved in a solution containing 17.05 g (230 mmol) 1-butanol, 2.39 g (38 mmol) HNO₃ and 2.37 g (4×10^{-5} mmol) Pluronic P-123. The mixture was stirred overnight at room temperature (RT) and dried in an oven at 120 °C for 6 h. The gel obtained was washed thrice with ethanol and centrifuged at 4200 rpm for 15 min interval, until the supernatant was clear, and subsequently, dried overnight in a vacuum oven at 70 °C. The powder obtained was subjected to various calcination cycles at 150 °C/12 h, 250 °C/4 h, 350 °C/3 h, 450 °C/2 h, and 550 °C/1 h. To obtain the best calcination temperature for the synthesis of the alkali doped supports, the H₂-TPR, and CO-TPR measurements were performed. Based on their respective low-temperature reducibility, the order follows thus: Co₃O₄-550 °C < Co₃O₄-450 °C < Co₃O₄-150 °C < Co₃O₄-250 °C.

The synthesis of the alkali metal-doped Co₃O₄ was carried out by a procedure earlier reported above. An appropriate amount of $x(NO_3)$ (x = K, Na, Li, Ca, and Cs) 2% (mol/mol) were added to a solution containing 5.82 g (20 mmol) of Co(NO₃)₂·6H₂O, 17.05 g (230 mmol) 1-butanol, 2.39 g (38 mmol) HNO₃ and 2.37 g (4 × 10⁻⁵ mmol) Pluronic P-123. The mixture was stirred overnight at RT and dried in an oven at 120 °C for 6 h. The product obtained was washed thrice with ethanol and centrifuged. The resulting powder was calcined at 350 °C for 3 h. Similarly, the temperature-programmed reduction measurements were used to obtain the best support for the synthesis of the catalysts. The order in their reduction temperature follows thus: Ca-Co₃O₄ < Li-Co₃O₄ < Na-Co₃O₄ < K-Co₃O₄ < Cs-Co₃O₄.

The gold nanoparticles were deposited on the mesoporous Cs-Co₃O₄ via the deposition-precipitation method with urea [52]. In a typical reaction procedure, 1 g of the Cs-Co₃O₄ was added to an aqueous solution of HAuCl₄.3H₂O and stirred for 1 h at room temperature. Urea in (2:1) molar ratio was added to the reaction mixture and heated to 80 °C. The solution was allowed to cool down, and freshly prepared NaBH₄ in (10:1) molar excess was added to the mixture and stirred for another 3 h. The resulting precipitate was filtered and washed with excess distilled water to remove the chloride. The catalyst was calcined at 350 °C for 3 h, and the initial Au loading was set at 5 wt.%.

2.3. Characterization of the catalyst

Scanning electron microscopy (SEM) was performed using a Tescan Vega 3 LMH instrument, operated at a high voltage of 20.0 kV. Before the analysis, the samples were carbon-coated in an Agar Turbo coater. Energy disperse X-ray spectroscopy (EDXS) on SEM, was used to determine the quantity of the dopants. Transmission electron microscopy (TEM) was carried out using a JEOL TEM-2100F, with an accelerating voltage of 200 kV. Prior to this, the catalysts were placed on the TEM-grids after ultrasonication in ethanol for 1 h. Powder X-ray diffraction (p-XRD) measurements were performed on a Philips XPERT-PRO diffractometer, operating with Cu K α 1 and K α 2 (λ -1.5406 and 1.54443), respectively. The scan ranges from $0.5-2^{\circ}$ and $10-80^{\circ}$ for the low and wide 2θ angles, respectively. Nitrogen sorption measurements were performed on a Micrometrics ASAP 2460 instrument at 77 K. Before the analysis; the samples were degassed at 80 °C under a nitrogen atmosphere and vacuum for 12 h and 3 h, respectively. The surface areas were calculated using a Brunauer-Emmett-Teller (BET) method. Temperature-programmed reduction (CO-TPR and H₂-TPR) were performed on a Micromeritics AutoChem II. The quartz tube reactor was loaded with about 45 mg of the catalyst and pretreated under argon/helium flow at 200 °C for 1 h. The materials were cooled and probed by passing 10% H₂/Ar (H₂-TPR) and 10% CO/He (CO-TPR) at different times through the catalyst bed at the flow rate of (50 mL min⁻¹), from room temperature to 700 °C (10 °C min⁻¹). Temperature-programmed desorption (CO₂-TPD) was performed on a Micromeritics AutoChem II, to determine the basicity of the catalysts. About 0.2 g of the catalyst was packed into a quartz tube reactor and pretreated under an inert gas (Ar) flow at 200 °C for 1 h. The materials were probed by passing 10% CO₂/He at a different time of measurements in the temperature range of 20-600 °C. A Spectro Arcos ICP-OES instrument was used to determine the metal loading (wt.%) of the nanomaterials. A TGA Perkin-Elmer STA 6000 instrument was used to carry out the thermogravimetric analyses with a ramping rate of 10 °C min⁻¹, from 25 °C to 1000 °C under nitrogen flow (100 mL min⁻¹). Fourier transform infrared spectroscopy (FT-IR) was conducted on a Shimadzu IRAffinity-1S, equipped with a QATR-10 single reflectance accessory, using KBr pellets in the region of 4000-500 cm⁻¹.

2.4. Catalytic reaction

Hydroformylation-hydrogenation reaction was conducted in a 100 mL Teflon tube inside a stainlesssteel Parr stirred reactor. In a typical procedure, 8 mmol of 1-octene, 8 mmol of decane (internal standard), and 40 mg of the catalyst were dissolved in 10 mL of the solvent and introduced into the reactor. The syngas H₂/CO (2:1) was set at 40 bar constant pressure, maintained throughout the reaction. The temperature was raised to 140 °C, with stirring and heating for 12 h. On completion of the reaction, the reactor was allowed to cool down. The products obtained were analyzed using gas chromatography (GC) mass spectroscopy (GC-MS) and a GC equipped with a flame ionization detector (FID). For recycling purposes, the catalyst was removed by centrifugation, washed successively with tetrahydrofuran (THF), and dried in a vacuum before reuse.

3.0 Results

3.1. Textural characterization of the mesoporous supports and catalysts

The structural properties of the nanomaterials are presented in Table 1 and Table S1. Nitrogen adsorption-desorption isotherms of the supports and catalysts are shown in Fig. 1, and Fig. S1, respectively. A Type IV isotherm and H1 hysteresis loop were observed for the nanomaterials, indicating a well ordered and regular uniform mesoporous structure of the materials [53], as observed from the quantity adsorbed at STP to the relative pressure (P/P₀) (Fig. 1a). As shown in Table 1, it is essential to note that upon doping the pure cobalt oxide, the average pore diameter increased, with a decrease in pore volume and surface area. Immobilization of the gold nanoparticles on the support (Cs-Co₃O₄) matrix further decreased the BET surface areas and pore sizes for the catalysts, with the least observed for 10% Au/Cs-Co₃O₄, and ascribed to the partial blockage of the mesopores due to the high metal loading content. The synthesized nanomaterials, as shown in Fig.1b, displayed a monomodal pore size distribution.

The powder X-ray diffraction patterns (p-XRD) for the nanomaterials are given in Fig. 1, and Fig. S2, and displayed a typical Co_3O_4 spinel pattern with cubic crystal structure [54]. The characteristics peaks and planes of the spinel Co_3O_4 could be well indexed in the JCPDS database (74-1657), indicating the purity of materials. Similar spectra patterns were observed for the cobalt oxide supports and catalysts at the different gold loadings (Fig. 1c). No distinct AuNPs reflection was seen for all the catalysts, indicating a small size or low content of the nanoparticles incorporated on to

support matrix, which could not be detected by the XRD, with no phase transition observed. The presence of sharp diffraction peaks in the low angle spectra is an indication of the existence of pores in the nanoscale for the materials [55] (Fig. 1d). Scherrer's equation was used to calculate the crystallite sizes of the nanomaterials, as shown in Table 1 and Table S1. It's important also to note that the crystallite size of the pure cobalt oxide increased upon dopping with alkali metals, and further increased on immobilization of the gold nanoparticles on to the support matrix.

Entry	Sample	Metal	Crystallite	Pore	Pore	SA_{BET}^{c}
			SIZES		$(am^3 a^{-1})$	(mg)
		(WL.%)	(nm)	(nm)	(cm ² g ⁻²)	
1	Co ₃ O ₄ -350 °C	-	7.4	12.8	0.36	64
2	Cs-Co ₃ O ₄	0.77 (Cs)	15.6	26.2	0.32	58
3	2% Au/Cs-Co ₃ O ₄	0.82 (Au)	18.2	24.9	0.29	52
4	5% Au/Cs-Co ₃ O ₄	4.71 (Au)	20.4	24.2	0.28	49
5	10% Au/Cs-Co ₃ O ₄	8.26 (Au)	26.7	9.1	0.21	22

 Table 1
 Textural parameters of supports and catalysts

^a Determined by ICP-OES. ^b Calculated using Scherrer's formula. ^c Determined by Nitrogen BET



Fig. 1. (a) Nitrogen-sorption isotherms, (b) BJH pore size distributions, (c) Wild angle, and (d) Low-angle p-XRD diffraction patterns of the supports and catalysts.

The morphologies of the nanomaterials were viewed by TEM and SEM, with the representative micrographs shown in Fig. 2. The Cs-Co₃O₄ showed an almost similar morphology to the 5% Au/Cs-Co₃O₄ catalyst, with a nano-sized ball-like particle (Fig. 2a and 2b), indicating that the gold nanoparticles did not alter the phase of the support. This was in good agreement with the p-XRD data, where the AuNPs were fully incorporated into the support matrix with the absence of new phases in the spectra. The HRTEM images in Fig. 2c and 2e, reveal the dispersed AuNPs with slight agglomeration on the cobalt oxide support, except for the 10% Au/Cs-Co₃O₄ catalyst, whose nanoparticles agglomerated more, due to the high metal loading on the support matrix (Fig. 2f). The particle diameters for the catalysts ranges from 2.1-8.8 nm, with 4.2 \pm 0.1 nm observed for 5% Au/Cs-Co₃O₄ and its corresponding size distribution shown in Fig. 2d. The lattice fringes of 0.24

nm, as revealed by the HRTEM image, can be well indexed to the (311) phase of a typical Co_3O_4 cubic spinel crystal structure. The representative AuNPs were indicated with a white circle.



Fig. 2. Representative SEM images of (a) Cs-Co₃O₄, and (b) 5% Au/Cs-Co₃O₄ and HRTEM images with particle size distribution of (c) (d) 5% Au/Cs-Co₃O₄, (e) 2% Au/Cs-Co₃O₄, and (f) 10% Au/Cs-Co₃O₄.

The temperature-programmed reduction is an efficient tool to determine the reducibility properties of nanomaterials. The supports and catalysts were analyzed by CO-TPR and H₂-TPR, and their respective profiles are presented in Fig. 3 and Fig. 4, with the data shown in Table 2. The CO-TPR

profile of the pure oxide Co₃O₄-350 °C shows two reduction peaks at 236 °C and 264 °C. On addition of the ion-promoter on Co₃O₄-350 °C, a significant reduction in temperature to 171°C and 241 °C was observed, indicating the easily reducible and electropositive nature of the alkali metal ions on the pure oxides [49] (Fig. 3a). The first profile peak at 171 °C, was ascribed to the reduction of Co₃O₄ to CoO, due to the reducible surface-active oxygen, and the peak at 241 °C can be attributed to the reduction of CoO to Co [56]. Fig. 3a shows a slight shift to lower reduction temperatures upon immobilization of the gold nanoparticles on the cobalt oxide support, except for 10% Au/Cs-Co₃O₄, which shifted to higher reduction temperatures at 274 and 334 °C, respectively. The inconsistency observed in the increased temperature values for 10% Au/Cs-Co₃O₄, was also in good agreement with BET data; we postulated that it might be due to the partial blockage of its mesopores from the increase in gold loadings on the support (Table 1). The notable decrease in the reduction temperature of the 5% Au/Cs-Co₃O₄ catalyst compared to Cs-Co₃O₄, shows that the gold nanoparticles promoted the spillover of CO on the support [57].

A similar trend in the reduction temperatures was observed for the H₂-TPR profiles of the nanomaterials (Fig. 4b). The supports and catalysts reduced in two stages, and are ascribed to the reducible surface absorbed capping oxygen and bulk reduction at a higher temperature, respectively. The shift to lower reduction temperature on the addition of ion-promoters and nanoparticles on the support, suggests an altered electronic structure upon immobilization. In the presence of the ion-promoters and nanoparticles, hydrogen atoms are more likely to be provided efficiently, and the probable reduction will occur at lower temperatures, as compared to the pure metal oxides without ion-promoters and nanoparticles in its matrix. This phenomenon is referred to as the hydrogen spillover effect [58,59].



Fig. 3. (a) CO-TPR and (b) H₂-TPR profiles of the supports and catalysts.

A comparison between the ion-promoted catalyst (5% Au/Cs-Co₃O₄) and its non-promoted counterpart (5% Au/Co₃O₄), shows the significant effect of the highly electropositive alkali metal ion (Cs) in the reduction temperature of the catalysts (Fig. 5). The lower temperature shift in the reduction peaks simply contributed to the high catalytic activity of the catalyst.



Fig. 4. Comparison of (a) CO-TPR and (b) H₂-TPR profiles of 5% Au/Co₃O₄ and 5% Au/Cs-Co₃O₄.

Entry	Samples	CO-TPR		H ₂ -TPR		Total basicity	
		(°C)		(°C)		$(mmol CO_2 g^{-1}) \ge 10^{-1}$	
		1 st	2 nd	1 st	2 nd		
1	Co ₃ O ₄ -350 °C	236	264	239	291	2.1	
2	Cs-Co ₃ O ₄	171	241	218	271	8.7	
3	2% Au/Cs-Co ₃ O ₄	164	198	208	267	9.3	
4	5% Au/Cs-Co ₃ O ₄	159	186	191	237	10.7	
5	10% Au/Cs-Co ₃ O ₄	274	334	282	319	4.3	

 Table 2
 Reduction temperatures and surface basicity of the nanomaterials

The relative basicity of nanomaterials is revealed by the CO₂-TPD analysis (Fig. 5), with the data summarized in Table 2. Alkali metal ions are known to increase the basicity of metal oxides and can enhance catalytic activity [49,60], due to their electropositive nature [61] and structural effects [51]. Strong broad peaks, high intensities, and more basic sites were observed for all the materials (2-5) at a temperature range of 96-452 °C, except for the pure metal oxide (1), which gave lower peak intensities. It should be noted that the immobilization of the AuNPs slightly improved the basic properties of the catalysts. As shown in Table 2, the amount of base concentrations of these nanomaterials ranges from 0.21-1.07 mmol g⁻¹, with the 5% Au/Cs-Co₃O₄ (5) showing the more pronounced base strength concentration of 1.07 mmol g⁻¹, highest peak intensities, and robust basic sites for probable activation of substrates. Therefore, we postulated that basicity played an essential role in these catalysts, which directly correlates and is in good agreement with the CO-TPR and H₂-TPR data.



Fig. 5. CO₂-TPD profiles of (1) Co₃O₄-350 °C, (2) Cs-Co₃O₄, (3) 2% Au/Cs-Co₃O₄, (4) 5% Au/Cs-Co₃O₄ and (5) 10% Au/Cs-Co₃O₄.

Fig. 6a shows the thermal stability of the nanomaterials evaluated by thermogravimetric analysis (TGA). All materials show a minor weight (%) loss in the range of 1.5-4.0% below 150 °C due to physically adsorbed moisture on the surface. At the second stage of degradation, a minimal weight loss was observed for the catalysts, except for Co_3O_4 -350 °C and Cs-Co₃O₄, which displayed weight loss at 69% and 54%, respectively. The weight loss in the range of 162-502 °C, is assigned to the thermal degradation of the organic matter in the catalysts, suggesting that these materials could safely be used well below 162 °C. The weight loss observed for Co_3O_4 -350 °C at 654 °C could be due to the decomposition of the inorganic residue.

The infrared spectra for the supports and catalysts are shown in Fig. 6b. All the as-synthesized nanomaterials gave the same peaks at around 659 and 561 cm⁻¹, assigned to Co-O stretching vibrations of the pure Co_3O_4 , which further confirms that the Cs and AuNPs did not alter the crystal structure of the spinel Co_3O_4 [62,63], and are well incorporated in its matrix. The FT-IR and p-XRD results unambiguously reveal that, after modification of the Co_3O_4 with Cs and AuNPs, its structure is retained, due to excellent dispersion on the support.



Fig. 6. Representative (a) TGA and (b) FT-IR spectra of the supports and catalysts.

3.2. Catalytic screening and activity for hydroformylation-hydrogenation of 1-octene.

The catalysts screening was performed under syngas H₂/CO (2:1) pressure for the hydroformylationhydrogenation of 1-octene (Table S2). The selected 1-octene was used as a screening molecule to understand the optimization of reaction conditions better. To further justify the promotional effects of the alkali metal ions on nanomaterials [49,51], the 5% Au/Co₃O₄ catalyst was compared with its ion-promoted counterpart (5% Au/Cs-Co₃O₄). The catalyst without alkali metal ions (5% Au/Co₃O₄), gave lower 1-octene conversion and alcohol selectivity to the ion-promoted catalyst (5% Au/Cs-Co₃O₄). Similarly, the pure metal oxide exhibited poor activity to the ion-promoted metal oxide. See Table S2 in the supplementary material. Furthermore, the effect of gold loadings on the catalyst was investigated. Under the same reaction conditions; 1-octene (8 mmol), catalyst (60 mg), H₂/CO 2:1, 40 bar, 140 °C, 16 h, THF (10 mL), the 5% Au/Cs-Co₃O₄ (1a) catalyst gave the best activity (92% conversion and 94% selectivity) to 10% Au/Cs-Co₃O₄ (58% conversion and 49% selectivity). The series in the activity of the catalysts were also in good agreement with the lowtemperature reducibility and surface basicity of the nanomaterials (Fig. 3, 4, and 5), which has an impact on the reaction turnover frequency (TOF). Thus, the observation due to the 1-octene conversion and selectivity to the desired alcohol is similar to the turnover frequency of the respective catalysts. The products of the 1-octene hydroformylation-hydrogenation were analyzed by GC-MS, indicating the mass charge (m/z) corresponds to nonanol. According to the GC-MS library, the fragmentation pattern matched the linear alcohol by 94%. Based on these results, the effect of reaction parameters using 5% Au/Cs-Co₃O₄ catalyst was studied.

3.2.1. Optimization of reaction conditions and substrate scope

The catalyst amount was varied from 20-80 mg, keeping other reaction conditions constant (Table 3). From observation, increasing the catalyst amount to 80 mg decreased the product selectivity slightly (Table 3, entry 4). On the other hand, reducing the catalyst amount to 40 mg did not show any significant effect on the reaction (Table 3, entry 2). A further decrease to 20 mg led to a considerable decrease in 1-octene conversion and alcohol selectivity (Table 3, entry 1). The temperature effect towards alcohol selectivity and 1-octene conversion was studied, respectively. The reaction temperature was varied from 120-160 °C. Interestingly, an increase in temperature to 160 °C, led to a significant decrease in the alcohol selectivity (77%) observed at a higher temperature of 160 °C, was due to the formation of the more hydrogenated substrate (octane) (Table 3, entry 7). At a lower temperature of 120 °C, the considerable decrease in alcohol selectivity (58%) was ascribed to isomerization and branched aldehyde formations (Table 3, entry 5).

From the carbon monoxide temperature-programmed reduction (Fig. 3a), the effect of carbon monoxide on the reduction behaviour of the catalysts suggests that CO improves the reducibility of cobalt-based catalysts [64]. As shown in Table S3, the effect of H_2/CO partial pressure was investigated. Lowering the pressure to 20 bar, gave poor 1-octene conversion and low alcohol selectivity (Table S3, entry 1). At pressure 40-60 bar, the branched aldehydes were fully converted to alcohol and hydrogenated substrates, with lower alcohol selectivity observed at 60 bar partial pressure (Table S3, entries 2-4). The reaction was successful under syngas H_2/CO (2:1), indicating that the excess hydrogen may have contributed to the formation of unsaturated [$HCo(CO)_y$] intermediates on the catalyst surface, for alcohol synthesis to proceed smoothly.

As shown in Table S3, entry 5, a significant decrease in 1-octene conversion, and alcohol selectivity was observed at 8h. At 16 h reaction time, the selectivity of alcohol reached 95%, with the highest turnover frequency achieved at 183 h⁻¹, for 1-octene hydroformylation-hydrogenation reaction (Table 3, entry 2). On further increase to 20 h (Table S3, entry 7), the conversion increased considerably with a slight decrease in the alcohol selectivity (85%). For different reaction time, the decrease in selectivity can be attributed to the formation of branched aldehyde and hydrogenated substrate products. The reaction rates for the 5% Au/Cs-Co₃O₄ catalyst at 140 °C and 40 bar, is shown in Fig. 7d. A first-order reaction with respect to 1-octene concentration was obtained from a straight-line plot of Ln(1-C_x) vs. time (*t*), with a -*k* slope, where Ln(1-C_x) = -0.16*t* + 0.03 and *k* is the first-order rate constant.

Using tetrahydrofuran as solvent resulted in the best activity compared to other solvents used in this study (Table S4, entry 3). The high activity could be ascribed to its ether functionality, which we believed to have played a vital role in the stabilization of the active species on the surface of the catalyst. Therefore, the hydroformylation-hydrogenation of 1-octene optimized reaction conditions are: 5% Au/Cs-Co₃O₄ (40 mg), 1-octene (8 mmol) H₂/CO (2:1, 40 bar), 16 hr at 140 °C in 10 mL THF.

To study the effect of the substrate structure on reactivity and to establish extensive applicability of this approach, the reactions of other alkenes were examined using the 5% Au/Cs-Co₃O₄ (**1a**) catalyst with the optimized reaction conditions. The use of the **1a** catalyst is due to the fact that it was the most active from the catalysts screening under the same reaction conditions (Table S2). From the data summarized in Table 3, the selectivity of alcohols decreased slightly with an increase in carbon chain lengths. For example, a 97% conversion with 98% alcohol selectivity was achieved for the hydroformylation-hydrogenation of 1-pentene in 16 hr at 140 °C (Table, entry 8). However, the selectivity decreased slightly to 96% for 1-hexene (Entry 9) and can be ascribed to faster formation of hydrogenated substrates. For styrene, a decrease in the product selectivity was observed (Entry 11).

The catalytic performance of 5% Au/Cs-Co₃O₄ was compared with other catalysts for the hydroformylation-hydrogenation of 1-octene (Table 4). The catalyst reported in [43], under syngas H₂/CO (2:1), gave 93% conversion with 87% selectivity to the desired alcohol at a pressure and temperature of 56 bar and 170 °C, respectively. The reusability of this catalyst reached three cycles, with a significant drop in conversion and selectivity. However, the ion-promoted catalyst reported in this present study was highly reusable, and exhibited higher alcohol selectivity under milder reaction conditions (120-140 °C and 40 bar), compared to other supported and homogeneous catalysts reported in the literature [41,43,65].

Entry	Cat. 1a	Temp.	Conversion		Selectivity		TOF
	(mg)	(°C)	(%) ^a		(%) ^a		(h^{-1})
				Aldehyde	Alcohol	(i:h) ^c	
				(l:b) ^b	(l:b) ^b		
1	20	140	78	29 (30:70)	42 (72:28)	07:22	81
2	40	140	92	00	95 (72:28)	00:05	183
3	60	140	92	00	94 (70:30)	00:06	181
4	80	140	95	00	88 (70:30)	05:07	169
5	40	120	63	22 (22:78)	58 (70:30)	08:12	111
6	40	150	94	00	91 (70:30)	00:09	175
7	40	160	96	00	77 (68:32)	00:23	148
8	40	140	97	00	98 (80:20)	00:02	189
9	40	140	91	00	96 (70:30)	00:04	185
10	40	140	88	00	96 (72:28)	00:04	185
11	40	140	83	00	92 (65:35)	00:18	177

 Table 3 Effect of catalyst amount, temperature and substrate scope

Reaction conditions: - 1-octene (8 mmol), H₂/CO (2:1), 40 bar, 16 h and THF (10 mL). Substrate scope: 40 bar, 16 h. 1-pentene (Entry 8), 1-hexene (Entry 9), 1-heptene (Entry 10), and styrene (Entry 11).

^a Selectivity and conversion.

^b Linear (l) and branch (b).

^c Hydrogenated (h) and isomerized substrate (i)



Fig. 7. Effect of (a) Catalyst amount, (b) Temperature, (c) Time and (d) Reaction rates for 1-octene hydroformylation-hydrogenation (where $C_x = \%$ conversion). Reaction conditions:- 1-octene (8 mmol), catalyst **1a**, H₂/CO (2:1), 40 bar, 16 h and THF (10 mL).

Catalyst	Conversion		Selectivity	Press.(bar)/Syngas	References
	(%)		(%)	$(H_2/CO)/$ Temp. (°C)	
		Aldehyde	Alcohol		
Co-SiO ₂	66.0	84.0	3.2	40/1:1/400	[58]
Co-Au/SiO ₂	70.6	85.4	3.1	40/1:1/400	[58]
Au/Co ₃ O ₄	99.5	83.9	4.4	40/1:1/130	[58]
Fibrous Co ₃ O ₄	93.0	-	87.0	58/1:2/170	[43]
Au/Co ₃ O ₄ /SiO ₂	100	28.0	41.0	90/1:2/120	[45]
$Co_2(CO)_8$	100	-	61	41/1:2/110	[41]
[Rh(CO)2acac]	81	-	77.0	50/1:2/120	[65]
5% Au/Cs-Co ₃ O ₄	92.0	-	95.0	40/1:2/140	Present study

Table 4 Catalytic activity for hydroformylation-hydrogenation of alkenes with other catalysts

3.2.2. Reusability study

The stability of a catalyst is a crucial requirement for its practical applications. Thus, the recycling of the 5% Au/Cs-Co₃O₄ catalyst for the hydroformylation-hydrogenation of 1-octene with syngas H₂/CO (2:1) was conducted. The 1-octene was used as the model molecule for the reaction. Catalyst separation was performed using simple filtration, washed thrice with THF, and heated in an oven at 250 °C for 1 h. The heating was done to remove the supernatant and reactivate the catalyst by reopening of the mesopores. The procedure was repeated before reusing the catalyst; this is in contrast to industrial homogeneous cobalt carbonyl-based catalysts, which forms insoluble cobalt precipitates under syngas pressure, due to its instability. As shown in Fig. 8a, the activity of the catalyst remained almost unchanged after four consecutive cycles, with the conversion and selectivity sustained at 88% and 83%, respectively, indicating its high reusability. Although, the slight decrease in alcohol selectivity observed was due to the formation of branched aldehyde and hydrogenated substrate products. The p-XRD spectra (before and after use) were also used to confirm these observations with not much difference observed, implying that the crystal structure of the used catalyst was preserved (Fig. 8b). To further confirm the presence of the absorbed species in the catalyst, the FT-IR analysis was carried out. Before this, the catalyst was removed, washed once with 15 mL THF and dried in a vacuum oven at 70 °C for 2 h. Fig. 8c showed the appearance of broad peaks at 3498 and 1722 cm⁻¹, assigned to alcohol (OH) and aldehyde (-C=O) stretching vibrations, respectively. The C-O bands at 2167 cm⁻¹ appeared in spectra, further confirming the presence of carbonyl like species on the catalyst surface [66]. Weak peaks at the range of 2978-3211 cm⁻¹ can be ascribed to the isomerized alkene (=C-H), alkane (-C-H), and aldehydic (-C-H) stretching bands. The metal bands (M-Co) at 561 and 659 cm⁻¹ also appeared in the spectra.



Fig. 8. (a) Reusability, (b) p-XRD (before and after use), and (c) FT-IR (before and after use) of 5% Au/Cs-Co₃O₄ catalyst.

4.0 Discussion

Mesoporous Co₃O₄ and its ion-promoted counterparts (Ca-Co₃O₄ < Li-Co₃O₄ < Na-Co₃O₄ < K-Co₃O₄ < Cs-Co₃O₄) were synthesized via inverse-micelle templated approach [46]. The hydrogen and carbon monoxide temperature-programmed reduction were used for optimization to obtain the best supports. The deposition-precipitation method was used for catalyst synthesis [52]. The HRTEM images reveal a slight agglomeration of the AuNPs on Cs-Co₃O₄. Irrespective of the gold loadings, the Cs-Co₃O₄ particles displayed an almost similar size around 15-30 nm, while the AuNPs sizes were markedly affected by gold loadings (Fig. 2). The 2 and 5% gold loadings, led to a low population of the AuNPs with sizes ranging from 2.1-6.0 nm on the support surface. In the case of

the 10% gold loading, the population of the AuNPs on the support surface increases (Fig. 2f). The pore structure and BET surface areas of the catalysts were also markedly affected by gold loadings, at 2, 5 and 10%, respectively (Table 1). The surface areas and pore sizes were observed to decrease on increasing the Au loadings from 2-5%, with the least observed for 10%, due to partial blockage of the pores. The catalytic data also reveals that an increase in gold loading up to 10 wt.%, significantly lower the activity for 1-octene hydroformylation-hydrogenation, and could be ascribed to the excess AuNPs in support matrix blocking the mesopores.

Fig. 8a shows that the insignificant decrease in 1-octene conversion and alcohol selectivity observed for each cycle can be ascribed to handling loss of the catalyst. To further determine the provisional release of the active sites from 5% Au/Cs-Co₃O₄, the heterogeneity test on the composite catalyst was performed for the hydroformylation-hydrogenation of 1-octene. Firstly, for the hot filtration test, the solid catalyst was filtered upon completion of the reaction, and the supernatant was returned to the reactor for 4 h keeping the optimized reaction conditions constant. The GC-FID results show that the 1-octene conversion after filtration increased, indicating slight leaching of the metallic cobalt into the reaction mixture, forming [HCo(CO)_v] specie that re-catalyzed the hydroformylationhydrogenation reaction (Fig. S8). In addition, the ICP-OES was used to analyze the filtrate after its fourth run and detected about 12.1 wt.% of the cobalt species in the solution. A comparison between the 5% Au/Co₃O₄ catalyst and its ion-promoted counterpart (5% Au/Cs-Co₃O₄) shows that the later was highly reusable and stable after its fourth run, despite both catalysts leached in the process. This further confirms the promotional effect of the alkali metal ions on the catalyst. See Fig.S9 in the supplementary material for the reusability studies. Therefore, a combination of the hot filtration test and reusability results reveal a little homogeneous contribution to the reaction due to the leaching observed. The cyclic ether functionality of the tetrahydrofuran solvent was believed to have played a significant role in the stabilization of the active species on the catalyst surface, which contributed to the conversion and selectivity. Another hypothesis that the active sites may be $[HCo(CO)_y]$ specie was confirmed by an immediate infrared analysis (Fig. 8c). A comparison between the fresh and used catalyst (5% Au/Cs-Co₃O₄) under the same reaction condition reveals that a new peak at 2167 cm⁻¹ due to the free C-O stretching vibrations appeared in the used catalyst, and can be assigned to cobalt carbonyl species [66]. This further supports the possibility that the active specie on the catalyst surface maybe $[HCo(CO)_y]$.

In this study, we believe the markedly enhanced catalytic activity of the catalyst, can be attributed to the generation of coordinatively unsaturated $[HCo(CO)_y]$ carbonyl-like species, formed via

spillover of H and CO by gold nanoparticles on the catalyst surface. Furthermore, to determine the reasons for the difference in the catalytic activity of the catalysts, the effect of reducibility temperature on the nanomaterials was studied in detail (Fig. 3). The catalyst with the highest H₂ and CO consumption at lower temperatures presented the best activity (Table 2, entry 4). Thus, the correlation observed indicates that the high consumption of CO and H₂ gas by the 5% Au/Cs-Co₃O₄ catalyst might be contributed to its high yield of alcohol (95%) formed for each of the studied catalysts. However, considering that the catalysts (5% Au/Cs-Co₃O₄ and 2% Au/Cs-Co₃O₄), almost possessed close reducibility temperatures, correlation with the high catalytic activities and high CO and H₂ consumption is not inevitable. Therefore, other determining factors for the high impact on catalytic activity is necessary. An evident correlation was found between the basicity (TPR-CO₂) and the reducibility temperature of the nanomaterials. The 5% Au/Cs-Co₃O₄ catalyst with more basic sites, presented the best activity to the other catalysts with smaller basic sites (Table 2). Thus, these findings further indicate that the AuNPs and alkali metal ions on the mesoporous support may have played an essential role in the increased basicity and temperature reducibility of the catalyst. We believe that the increase in the basicity of the ion-promoted catalyst, also facilitates the increase in adsorption sites of the materials [49], thereby promoting the rapid activation of the syngas and substrate on the catalyst, for hydroformylation-hydrogenation reaction to proceed smoothly. In the case of the pure oxide (Co₃O₄-350 °C) investigated under this study, its low catalytic activity may be ascribed to its higher reducibility temperatures (Table 2, entry 1), poor basic sites and absence of AuNPs to promote H/CO spillover in the formation of the surface-active [HCo(CO)_v] specie. Thus, with the correlation between the surface basicity, temperature reducibility of the catalyst, and the formation of [HCo(CO)_y] specie, we propose a reaction mechanism for 1-octene hydroformylationhydrogenation with $H_2/CO(2:1)$ (Fig. 9).

The mechanism involves different steps. In the first step (1), the significant role of the AuNPs in the catalyst is assumed to provide spillover of hydrogen and carbon monoxide on its surface, in the *insitu* reduction of the Co_3O_4 to Co metal. The reduction behaviour of the H and CO was also evident from the temperature reducibility experiments (Fig. 3a and b). Furthermore, the Co metal combines with the hydrogen and carbon monoxide to form the surface-active species $[HCo(CO)_y]$ (1a). At step (2), an alkyl-metal complex (2a) is formed via alkene-metal complexation from the 1-octene (1a¹) interaction with the active surface. The alkyl-metal undergoes hydrogenation via reduction to form the surface-active catalyst interacts via insertion with the alkyl-metal to form an acyl-metal complex (3a). If the absorbed CO on the active surface does not interact with the alkyl group to form the acyl

complex, the 1-octene hydroformylation-hydrogenation reaction may not have progressed smoothly. In step (4), hydride transfer with the acyl-metal complex gives an aldehyde (4a), which undergoes hydrogenation to form the linear alcohol product (nonanol) (4 a^1). Branched alcohol (3-methyloctanol), was assumed to be formed via similar reaction pathway in Fig. 9.



Fig. 9. The plausible reaction mechanism for hydroformylation-hydrogenation of 1-octene on 5% Au/Cs-Co₃O₄ catalyst

5.0 Conclusion

Mesoporous M-Co₃O₄ and Au/M-Co₃O₄ catalysts (M= Ca, Li, Na, K, and Cs) have been successfully synthesized via inverse-micelle and deposition-precipitation methods, respectively, for the hydroformylation-hydrogenation of 1-octene to nonanol, under syngas H₂/CO (2:1) pressure. The catalytic activity was markedly affected by gold loadings (2, 5 and 10%) and the presence of alkali ion-promoters on the support matrix. The 5% Au/Cs-Co₃O₄ catalyst was more active than the other synthesized catalysts, with selectivity to the desired alcohol achieved at above 90% under milder reaction conditions (120-140 °C and 20-40 bar). The significant role of the AuNPs was assumed to provide CO and H spillover in the *in-situ* reduction of the mesoporous cobalt oxides to metallic cobalt forming carbonyl complex specie [HCo(CO)_y], that catalyzed the reaction. The

tetrahydrofuran gave the best activity as compared to the other solvents and believed to have played a vital role in the stabilization of the active species on the catalyst surface. The stability of the catalyst was retained after four consecutive cycles and could be used as a natural handling alternative to industrial cobalt carbonyl complexes, which requires rigorous purification processes. In summary, the synthesized cobalt-based catalyst has proven to be more advantageous to its homogeneous counterpart, in terms of activity, reusability, process handling, catalyst recovery, and could effectively carry out the hydroformylation-hydrogenation of alkenes to alcohols. The various characterization tools employed for the catalysts provided an extensive understanding of the reaction mechanism and catalyst evolution, which could find applications in the conversions of other alkenerelated compounds for value-added chemical synthesis.

CRediT statement

COO: Investigation; Formal analysis; Methodology; Writing - original draft; Writing - review & editing

BMM: Formal analysis; Methodology

CAA: Formal analysis; Methodology

RM: Conceptualisation; Methodology; Resources; Writing – review & editing; Supervision; Project administration; Funding acquisition.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of interest

The authors declare no competing financial interest

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