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Mesoporous Co₃O₄ Catalysts for VOC Elimination: Oxidation of 2-propanol

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Highlights

- Mesoporous Co₃O₄ showed high activity for elimination of 2-propanol at low temperature.
- Better low temperature reducibility, large pore volumes, higher Co³⁺/ Co²⁺ amounts, and higher number of surface-active oxygen species are crucial for higher activity.
- Reaction involves formation of carbonyl and carbonate species on the surface of the catalyst before complete oxidation to CO₂ and H₂O.
- Long term durability and maintaining activity in the presence of water and carbon dioxide make these catalysts attractive.
- The developed catalytic protocol sheds light on non-precious metal catalysts for VOC elimination.

Abstract

Mesoporous cobalt oxides were prepared by an inverse micelle method and calcined at different temperatures. These materials exhibited superior activity for oxidation of 2-propanol as the model substrate for VOC elimination. Highest active Co_3O_4 -350 material showed a maximum turnover frequency of 25.8 h⁻¹ at 160 °C at a weight hourly space velocity of 60 L g⁻¹ h⁻¹. The apparent activation energies of mesoporous cobalt oxides ranged from 69.7 kJ/mol to 115.6 kJ/mol. *In situ* Diffuse Reflectance Infrared spectroscopy (DRIFTS) revealed that the reaction involves formation of carbonyl and carbonate species on the surface of the catalyst before complete oxidation to CO₂ and H₂O. The activities of the materials were correlated to better low temperature reducibility, large pore volumes, higher Co^{3+}/Co^{2+} ratios, and higher number of surface-active oxygen species.

Keywords: Mesoporous Co3O4; Catalysis; 2-propanol; VOCs oxidation

1. Introduction

Volatile organic compounds (VOCs) are identified as major contributors of global air pollution[1],[2],[3],[4]. These compounds are precursors for the formation of ozone, photochemical smog, and secondary aerosols [5],[6],[7]. They are released to the environment by a variety of methods such as industrial processes, transportation, and domestic activities.

Industrial processes are comprised of chemical, power and pharmaceutical plants, gas stations, petroleum refining, printing, shoemaking, food processing, automobile, furniture, and textile manufacturing [8],[9],[10]. VOCs are the most plentiful and malignant chemical toxins in indoor air. In addition, most VOCs are further recognized as carcinogens, mutagens, and teratogens to humans [11],[12],[13].

Stern control of the VOCs evolved is required due to the extremely adverse effect of VOCs on the environment and human health, in addition to the humongous boost in the extent of these emitted compounds. Therefore, techniques and materials to moderate the levels of VOCs are in high demand. Condensation, incineration, biological degradation, adsorption, and absorption are typical processes for VOC elimination [14]. However, catalytic oxidation which transforms these toxic compounds to CO₂ and H₂O is well accepted as one of the most up and coming technologies for VOC abatement [15],[16],[17]. The utilized catalysts drop the activation energy of the reactions and total oxidation of pollutants occurs at lower temperatures in comparison to thermal combustion. Another benefit of catalytic oxidation is the use for odor regulation and treatment of emissions with evaporated solvents [18],[19]. Control of temperature for catalytic oxidation using exceptionally efficacious catalysts is a field studied extensively in recent years. Two leading types of catalysts used are noble metal supported catalysts and transition metal oxides [20],[21]. In comparison with scarce noble metals, transition metal oxides are much more inexpensive, practical, and active in some reactions [3],[14]. In terms of transition metal oxides, cobalt oxides have been demonstrated to be efficient catalysts for VOC destruction [17], [22]. They have equivalent activities to noble metals and supported noble metals making them a cheaper substitute [23],[24],[25].

Cobalt (II,III) oxide (Co₃O₄) exhibits a spinel structure and has a unit cell length of 0.8084 nm. As far as the unit cell is considered, lattice oxygens are cubic close packed where Co²⁺ possesses one-eighth of the tetrahedral sites and Co³⁺ possesses half of the octahedral sites [26]. Co₃O₄ materials have been synthesized by a variety of methods and the surface area, surface active oxygen species, exposure to active crystal facets, and Co³⁺ ionic species are reasons for high activity [27],[28]. Co₃O₄ is utilized as an effective catalyst for oxidation of CO[29],[30], CH4[31],[32], C₂H₂[28],[33], C₃H₈[34],[35], C₇H₈[24],[36], and chlorinated VOCs [22],[37]. The activity of Co₃O₄ in elimination of the oxygenated VOC 2-propanol has not been reported. Nonetheless, oxidation of 2- propanol has been studied with modified perovskite

catalysts.[16],[17],[38] Furthermore, most of the above reported materials were synthesized by hard template or precipitation methods. Therefore, it is a necessity to investigate the activity of Co₃O₄ synthesized by other methods such as the soft template inverse micelle method which gives diverse properties to materials for oxygenated VOC removal.

In this study, well-ordered mesoporous cobalt oxides have been synthesized using an inverse micelle strategy developed by our group which minimizes surfactant inorganic interactions and solvent involved interactions. A unique NOx chemistry is employed to control the hydrolysis and condensation of the oxo clusters which ultimately produces mesoporous materials with monomodal pore size distributions and crystalline pore walls. Unique redox properties, high surface area, and tunable porosity of these materials were the reasons for concentrating on cobalt oxide synthesized by this evaporation induced self-assembly method. We report the outstanding activity of mesoporous cobalt oxide materials for oxidation of 2-propanol under oxygen deficient conditions. These materials maintain the catalytic activity in the presence of water vapor (3%) and carbon dioxide (0.9%) in the feed gas. Intensified redox properties and adjustable porosity of these materials improve the catalytic activity by reducing the solid state diffusion distances [39]. The synthesized catalysts were characterized with powder X-ray diffraction (PXRD), N₂ sorption, X ray photoelectron spectroscopy (XPS), hydrogen temperature programmed reductions (H₂ TPR), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM). Furthermore, cross sections of the nano clusters were examined by TEM using a focused ion beam to prepare the samples. These characterization techniques were utilized in order to probe factors that influence the catalytic activity by establishing possible links between physicochemical properties of these materials and catalytic activities.

2. Experimental Section

2.1 Chemicals

Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, \geq 98.0%), 1-butanol (anhydrous, 99.8%), poly-(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol) (PEO₂₀-PPO₇₀-

PEO₂₀, Pluronic, P123), and concentrated sulfuric acid(H₂SO₄, 95–98%) were purchased from Sigma-Aldrich. Commercial cobalt oxide (bulk Co₃O₄) purchased from Stremchem Chemical Inc. company was 99.5% in purity. Concentrated nitric acid (HNO₃, 68–70%) and 2-propanol were purchased from J.T. Baker. All chemicals were directly used as received without further purification.

2.2 Catalyst Synthesis

The synthesis was done by dissolving 0.0017 mol of $Co(NO_3)_2$. 6H₂O in a solution containing 0.33 mol of 1- butanol, 0.038 mol of HNO₃ and 4.31×10^{-4} mol of P123 in a 150 mL beaker. A clear gel was formed after magnetic stirring at room temperature which was placed in an oven at 120 °C for 3 h. Then the product was washed with ethanol four times, centrifuged, and dried in a vacuum oven. Powders obtained were calcined at 150 °C for 12 h with a heating ramp of 10 °C per minute.

These samples were further calcined at 250 °C, 350 °C, and 450 °C for 3 h with a heating ramp of

2 °C per minute and samples were named as Co₃O₄-X (X=150, 250, 350, and 450) respectively.

2.3 Material Characterization

Powder X-ray Diffraction XRD studies were done on a Rigaku Ultima IV diffractometer using Cu K α (λ =0.15406 nm). A beam voltage of 40 kV, and 40 mA was used. Wide angle PXRD diffraction patterns were collected over a 2 θ range of 10° –75°. The nitrogen sorption experiments were done using a Quantachrome Autosorb iQ₂ automated sorption system. All samples were degassed at 150 °C for 5 h under vacuum prior to the nitrogen sorption experiment. The Brunauer-Emmett-Teller (BET) method was used for the surface area analysis and the Barrett-Joyner-Halenda (BJH) method was used on the desorption branch of the isotherm to determine the pore size distribution.

The morphologies of the metal oxides were studied using a FEI Nova Nano SEM 450 FESEM with a Schottky emitter at an accelerating voltage of 2.0 kV and a beam current of 1 mA. TEM, HR TEM and selected area electron diffraction (SAED) images were collected using a Talos F200X microscope operating at 200 kV. FIB sample preparation was done using an FEI Helios 460F1 FIB. H₂ TPR experiments were conducted in a Thermolyne 79300 model temperature

programmable tube furnace equipped with a Cirrus MKS Residual Gas Analyzer with a quadrupole mass selective detector. About 100 mg of the catalyst was packed into a quartz tube reactor which was mounted into a furnace. After that, physisorbed gases were removed from the catalyst surface by using a 50 sccm Ar flow for 30 minutes at room temperature. Finally, the catalysts were heated under a steady flow of 5% H₂ in He gas mixture from 100 °C to 700 °C at a ramp rate of 10 °C min⁻¹ for desorption. TPD experiments were conducted with the use of Ar (20 sccm) using the same set up. XPS was carried out on a PHI model 590 spectrometer with multiprobes (Φ Physical Electronics Industries Inc.). Al-K α radiation ($\lambda = 1486.6 \text{ eV}$) was used as the radiation source. Binding energies were measured for C 1s, O 1s, and Co 2p transitions. The binding energy value of 284.6 eV for C 1s was used to calibrate binding energies. In situ diffuse reflectance infrared spectroscopy (In situ DRIFTS) was performed on a Nicolet 8700 FTIR spectrometer with an In situ cell to clarify the intermediate species during 2propanol oxidation and its mechanism. The catalyst was packed into the sample holder. After that, physisorbed gases were removed from the catalyst surface by using a 100 sccm He flow for 30 minutes at 150 °C. After that, samples were pretreated with He for one hour at 150 °C. Then 2-propanol was introduced to the catalysts by passing ultra-zero grade air through a 2-propanol bubbler for 15 minutes at a flow rate of 20 sccm. Next, the catalyst was heated from 100 °C to 350 °C with an air atmosphere. All spectra were recorded with a 4 cm⁻¹ resolution and 64 scans.

2.4 Catalytic activity tests

The oxidation of 2-propanol over cobalt oxide materials was carried out in a fixed bed flow type quartz tube reactor (~ 0.4 cm internal diameter) under atmospheric pressure. About 100 mg of the catalyst was loaded in the middle of the quartz reactor supported by quartz wool and pretreated with flowing UHP He (50 sccm) for 1 h at 200 °C to clean the catalyst surface. Ultrazero grade air (21 % O₂) was bubbled in the 300 mL solution of 2-propanol at a flow rate of 20 sccm using a MKS digital mass controller to carry out the catalytic reaction giving a weight hourly space velocity (WHSV) of 12 Lh⁻¹g⁻¹. The temperature range for the reaction was 100-340 °C. Reaction products were analyzed after a stabilization time of ~20 minutes on stream. The product gas stream was analyzed online after passing through a cold trap (dry ice) with SRI 8610C gas chromatographs (GC) equipped with a thermal conductivity detector (TCD), flame ionization detector (FID), a 6-foot-long molecular sieve 13X packed column, and a 6-foot-long

silica gel packed column, and a 6-foot-long Haysep D packed column. Helium was used as the carrier gas of the GC. The organic products collected in the cold trap were analyzed on an 7820A GC system equipped with a mass selective detector 5975 series from Agilent Technologies. 2-propanol concentrations of the feed gas and the reactor outflow were calculated using the moles of oxygen reacted. The oxygen consumption was calculated based on oxygen concentration which was calculated using nitrogen as an internal standard [18]. The effect of water vapor was studied by using a bubbler with 1:1 volume ratio of 2-propanol to water (3% water vapor) in the stream at 25 °C. Carbon dioxide (0.9% CO₂) was introduced by bubbling 1% CO₂ balanced with air through 2-propanol. Saturated vapor pressures of 2-propanol at 25 °C and corresponding flow rates of air in an open system (1 atm and 25 °C) were used to calculate the initial concentration of 2-propanol.

3. Results

3.1 Characterization of mesoporous cobalt oxide catalysts

3.1.1 Powder X-ray diffraction (PXRD)

The PXRD patterns for the synthesized mesoporous cobalt oxides calcined at 150 °C, 250 °C, 350 °C, and 450 °C together with the commercial material are given in **Figure 1**. All materials except Co₃O₄-150 conformed to the spinel Co₃O₄ crystalline pattern (JCPDS 01 043 1003). Co₃O₄-150 showed diffraction lines that can be indexed to a mixed phase of Co₃O₄ and cobalt acetate hydrate (C₄H₆CoO₄·4H₂O). However, after calcination at 250 °C the crystal structure was completely transformed to Co₃O₄. When the catalysts calcined at 250 °C, 350 °C, and 450 °C are considered, the wide angle PXRD peak intensities and sharpness gradually increased with increasing calcination temperatures. The highest intensity and the sharpest peaks were observed for the commercial sample. The peak intensity is a measure of the crystallinity whereas the sharpness is a measure of crystallite size. Therefore, the crystallinity and crystallite size increase as the calcination temperature increases from 250 °C to 450 °C and the commercial sample has the highest crystallinity and crystallite size.



Figure 1. Wide angle powder X-ray diffraction patterns of mesoporous cobalt oxide materials and commercial Co₃O₄ material.

3.1.2 N₂ Sorption

Figure 2 shows the nitrogen sorption isotherms of the mesoporous cobalt oxide materials together with the bulk cobalt oxide material. BET surface areas, BJH pore volumes, and pore diameters are summarized in **Table 1**. The Co₃O₄-150 shows a type III adsorption isotherm indicating the nonporous nature of the samples. The curve is convex to the P/Po axis at higher relative pressure values. On the contrary, Co₃O₄-250, Co₃O₄-350, and Co₃O₄-450 demonstrate type IV adsorption isotherms with an H1 hysteresis loop [40]. The occurrence of pore condensation is implied by the hysteresis loops. This is an indication of the existence of an ordered mesoporous structure. The highest surface area is for Co₃O₄-250 (121 m²/g). As the calcination temperature is raised the surface areas decrease for the materials calcined at 350 °C

(83 m²/g) and 450 °C (36 m²/g). The bulk Co_3O_4 shows a type III adsorption isotherm indicating the nonporous nature of the samples and surface areas of the mesoporous materials are significantly higher compared to the bulk material (3 m²/g).



Figure 2. N₂ sorption measurements: (a) N₂ sorption isotherm, (b) BJH pore size distributions.

The BJH pore sizes assuming cylindrical pores are given in **Figure 2** (b). When the materials calcined at 250 °C, 350 °C and 450 °C are considered, the pore sizes increased as the calcination temperature increases implying that the pores expand as the calcination temperatures increase. BJH pore volume is highest for $C_{03}O_{4}$ -350 (0.331 cc/g).

Table 1.

Physical properties and surface elemental analysis of the catalysts discussed in the manuscript.

Material	Surface area (m²/g)	BJH pore volume (cc/g)	BJH pore diameter (nm)	^a Co ³⁺ /Co ²⁺	^a O _{ads} /O _{latt}
$Co_3O_4 - 150$	7	0.034	1.4	-	
$Co_{3}O_{4} - 250$	121	0.284	6.6	2.50	0.67
$Co_3O_4 - 350$	83	0.331	9.6	2.63	0.90
$Co_{3}O_{4} - 450$	36	0.237	17.9	2.00	0.58
Co ₃ O ₄ – Bulk	3	0.057	1.7		-

^a Determined from XPS spectra. - Not determined.

3.1.3 Scanning electron microscopy

Scanning electron microscopy and transmission electron microscopy were used to study the morphology of the materials. **Figure 3** gives the SEM images of the mesoporous cobalt oxide samples. The morphology of the samples consists of spherical clusters with nano size plates. The opening of the pores are increased with heat treatment. The cluster diameter is about 3 μ m. The rod length is around 1 μ m and width is about 200 nm. The enhancement of the pores with heat treatment could be observed by the SEM images. The uniform porosity of the material calcined at 450 °C is visible.



Figure 3. Scanning electron microscope images of mesoporous cobalt oxide. (a) Co_3O_4 -150 (b) Co_3O_4 -250 (c) Co_3O_4 -350 (d) Co_3O_4 -450.

3.1.4 Transmission electron microscopy

Figure 4 shows the TEM and HRTEM images of the mesoporous cobalt oxide materials. TEM analysis reveals obvious size changes of the materials upon increasing calcination temperature. The particle sizes were 4.6 ± 0.9 nm, 9.0 ± 1.8 nm, and 14.3 ± 1.9 nm for the calcination temperatures 250 °C, 350 °C, and 450 °C respectively. The HR TEM images of Co₃O₄-350 give insight to the mesopores in the material. These images show crystalline pore walls with well-defined lattice fringes. The nanoparticles acquire a polyhedral shape. Furthermore, they are randomly packed to form the mesoporous network. This confirms the crystalline nature of the nanoparticles. The d spacing values of cobalt oxide calcined at 350 °C turned out to be 0.46, 0.28, 0.24, and 0.20 corresponding to (111), (220), (311), and (400) planes respectively. Phase identification was done from SAED images from regions of the Co₃O₄-350 particles by calculating the lattice spacing and then were comparing with the JCPDS values (JCPDS 01 043 1003) as shown in **Figure 4**. SAED patterns reveal the pure crystalline nature of the annealed particles with cubic crystal structure, where (111), (220), (311), (400), (511), and (440) lattice planes were clearly indexed in agreement with the PXRD data. **Figure S1** shows the

FIB prepared TEM images of the mesoporous cobalt oxide materials. Feather like morphology is seen inside the nanoclusters. These images show the origin of the mesoporosity of the material. FIB prepared HR-TEM images confirm the mesopores inside the spherical nanoclusters.



Figure 4. Transmission electron microscope images of (a) Co₃O₄-250, (b) Co₃O₄-350, (c) Co₃O₄-450, (d) FIB-TEM Co₃O₄-350, (e) HR TEM Co₃O₄-350, (f) SAED pattern of Co₃O₄-350.

3.1.5. H₂ Temperature programmed reduction

H₂ temperature programmed reduction was done in order to evaluate the redox properties of the materials (**Figure 5**). The reducibility of as prepared samples was evaluated by H₂ TPR to differentiate the activity of surface oxygen. Generally, the reduction of cobalt oxide is known to occur through two steps. At lower temperature Co_3O_4 is first reduced to CoO followed by a second reduction step of CoO to Co at higher temperature [23], [24], [41], [42]. The first reduction peaks of Co_3O_4 -350, Co_3O_4 -250, Co_3O_4 -450, and Co_3O_4 -bulk are 273, 305, 326, and 380 °C

respectively. Therefore, Co₃O₄-350 showed the lowest onset reduction temperature among all samples.



Figure 5. H₂ TPR profiles of Co₃O₄-250, Co₃O₄-350, Co₃O₄-450, and Co₃O₄-Bulk.

3.1.6. Catalytic activity evaluation

Turnover frequency (TOF) vs temperature profiles of the mesoporous materials were used to evaluate the catalytic performance for 2-propanol oxidation. Commercial cobalt oxide is also included for comparison. The catalytic activities are compared by means of reaction temperature at which the TOF of 2-propanol is 10%, 50%, and 90% of the maximum TOF achievable. **Table 2** summarizes the catalytic performance of the materials. No CO was detected in all catalytic experiments and minute amounts of acetone was detected in the cold trap under experimental conditions. The carbon balance between 2-propanol and total oxidation product CO₂ was found to be over 90%.

The catalytic activity was evaluated at 12 L g⁻¹ h⁻¹ and 60 L g⁻¹ h⁻¹ weight hourly space velocity (WHSV) values. The light off curves of the cobalt oxides at these WHSV are given in **Figures 6 (a)** and **Figure 6 (b).** As far as the lower WHSV is considered, mesoporous cobalt oxides are more active (Lower T10 temperature) compared to the non-porous cobalt oxide material. The order of T10 temperatures increases in the order: Co_3O_4 -350 < Co_3O_4 -250 < Co_3O_4 -450 < Co_3O_4 -Bulk. T90 values increase in the order Co_3O_4 -350 < Co_3O_4 -250 < Co_3O_4 -450 < Co_3O_4 -Bulk. T90 values increase in the order Co_3O_4 -350 < Co_3O_4 -250 < Co_3O_4 -450 < Co_3O_4 -Bulk. The order of T10 and T90 follows the same trend at a WHSV of 60 L g⁻¹ h⁻¹ as shown in **Figure 6 (b).** Obviously, mesoporous materials show lower light off temperatures and the material calcined at 350 °C exhibits the highest activity at both lower and higher WHSV values.

Moles of 2-propanol converted were determined by the concentration change as well as the simultaneous CO_2 generation and these results are shown in **Figure S5a and S5b**. These plots emphasize the simultaneous generation of carbon dioxide with the conversion of 2-propanol. Furthermore, the catalytic activity follows the same trend as above. Moreover, we considered varying percentages of oxygen in the gas stream (21,30, and 40%) at 200 °C where at 40% oxygen 2-propanol becomes the limiting reagent. Here, the total amount of 2-propanol (6.4%) in the gas stream gets converted to CO_2 (**Figure S5c**).

CoMn₂O₄ catalysts have been reported for 2-propanol oxidation and complete conversion with only 0.2% propanol in the stream was achieved at 350 °C [17]. CoCr₂O₄ catalysts have been reported for the complete conversion of 2-propanol at 300 °C under similar conditions [38]. Furthermore, Au/CeO₂ catalysts have been reported for 2-propanol elimination with only 1 mol% 2-propanol at 150 °C [43]. Compared to these literature data which even use noble metals as catalysts, the findings presented here of 4.7% of 2-propanol conversion is promising.

3.1.7. Kinetic Studies

The onset of 2-propanol oxidation is governed by the kinetics of the reaction. To investigate the kinetics, apparent activation energies were calculated when oxygen conversion was lower than 20%. Due to the importance of mass and heat transfer, the operating temperatures are lower than light off temperatures [44],[45]. Moreover, at low oxygen conversions mass diffusion limitations can be considered as negligible [45],[46]. Apparent activation energy can be utilized to evaluate the catalytic performance of materials in a reaction and calculated values

based on Arrhenius plots given in **Figure 6** (c) are shown in **Table 2**. The calculated apparent activation energies for the catalysts follow the order Co_3O_4 -350 (69.7 kJ/mol) < Co_3O_4 -250 (108.9 kJ/mol) < Co_3O_4 -450 (115.6 kJ/mol) This trend is perfectly in line with the increasing order of T90 temperatures of the catalysts. The lower the Ea value, the more feasible the oxidation of 2-propanol. This result obtained from the kinetic experiment is consistent with the performance of the catalysts. The activation energy for the mesoporous materials are much lower than the bulk materials. This is proof of the lack of gas diffusion limitations in materials with mesopores [18].



Figure 6 Activity of cobalt oxides for 2-propanol oxidation. (a) 6.4% 2-propanol in air, WHSV 12 L g⁻¹ h⁻¹ (b) 6.4% 2-propanol in air WHSV 60 L g⁻¹ h⁻¹. TOF = moles of 2 propanol converted per hour/ moles of catalyst. (c) Arrhenius plots and apparent activation energy calculations with 6.4% 2 propanol in air WHSV 60 L g⁻¹ h⁻¹ (d) Activity for 2-propanol oxidation under the presence of 3% H₂O and 0.9 %CO₂ with 6.4% 2-propanol in air, WHSV 12 L g⁻¹ h⁻¹.

Material	T ₁₀ (°C)		T50(°C)		T90(°C)		^c Ea (kJ/mol)
	a	b	a	b	а	b	-
Co ₃ O ₄ -250	140	160	171	168	192	177	108.9
Co ₃ O ₄ -350	128	137	148	149	158	157	69.7
Co ₃ O ₄ -450	199	174	209	188	218	196	115.6
Co ₃ O ₄ -Bulk	241	197	250	209	259	217	180.2

Table 2. Summary of catalytic activity and calculated activation energies (Ea).

^a WHSV 12 L g⁻¹ h⁻¹. ^b WHSV 60 L g⁻¹ h⁻¹. ^c WHSV 60 L g⁻¹ h⁻¹ and calculated from the Arrhenius plots for 2-propanol conversion with oxygen conversion below 20%.

3.1.8. Effect of water vapor, carbon dioxide, and results of the stability test

The 2-propanol oxidation under moisture rich conditions (~3%) was performed for the cobalt oxide calcined at 350 °C at WHSV 12 L g⁻¹ h⁻¹. After sending about 3% moisture into the feed gas stream, The T90 of the catalyst shifts slightly to a higher temperature of 165 °C from 157 °C (**Figure 6 (d)**). Furthermore, the catalytic activity after introducing 0.9% CO₂ in a WHSV of 12 L g⁻¹ h⁻¹ was evaluated. Here the T90 temperature shifted to 178 °C. The catalytic stability tests were conducted on Co₃O₄-350 to investigate whether the catalysts were deactivated under the feed gas stream. As shown in **Figure S2** Co₃O₄-350 was extremely stable for 2-propanol oxidation at 240 °C. No decrease in activity was observed for ~48 h (~2 d) as far as the Co₃O₄-350 material is considered.

The sample did not show any transformations according to the PXRD analyses after the stability tests. Similar PXRD patterns were observed for the catalyst before and after the stability tests as shown in **Figure 7** (a). This indicates that the material is thermally stable under experimental conditions. The morphology of the material after the stability test was observed using TEM and SEM (**Figure S2**). No significant change was observed by TEM and SEM as

compared to the fresh catalyst. The absence of phase transformations and segregation were confirmed by HR-TEM images by the clear lattice fringes. The exposure to high temperature for a longer period of time does not change the structure or the morphology of the material. Temperature programmed desorption was carried out for the Co₃O₄-350 after being tested for stability. This was done in order to identify the species that were adsorbed on the catalysts after 48 h of reaction. **Figure 7 (b)** shows the results obtained in this experiment. The only gas desorbed in the experiment is carbon dioxide (327 °C). This can be attributed to the dissociation of carbonate species that may be formed during the reaction.



Figure 7. (a) PXRD patterns of Co₃O₄-350 before and after the stability test. (b) CO₂ TPD after stability test.

PXRD patterns of the catalysts were collected after the activity measurements (**Figure S4**) and the patterns showed a mixed phase consisting of CoO and Co₃O₄. The intensity of the Co₃O₄ peaks became less and peaks of CoO appeared. This indicates that the materials get reduced when 2-propanol is oxidized as the reaction temperature is increased to 340 °C. The stability test confirms that there is no reduction of the material at 240 °C. TPO experiments were done for the catalysts after the reaction to notice any coke formation during the reaction. No peak was observed for carbon dioxide indicating that there is no coke formation during the reaction.

3.1.10. X-ray photo electronic spectroscopy

XPS is a technique which is based on the photoelectric effect whereby energy of the incident photons is expended in the ejection of a photoelectron. This is a useful technique to study the

surface composition, metal valence states, and local atomic environments of a material. **Figure 8** shows the XPS spectra of the mesoporous cobalt oxide materials. The presence of Co₃O₄ is confirmed by Co 2p_{3/2} and Co 2p_{1/2} peaks appearing at about 780.0 eV and 795.0 eV respectively. Since valence states of cobalt may have a high impact on catalytic activity, the Co $2p_{3/2}$ peak was deconvoluted to Co²⁺ and Co³⁺ peaks as shown in **Figure 8** (a). The Co 2p peaks at binding energies of ~779.6 eV and ~794.7 eV are characteristic of Co³⁺ whereas Co 2p peaks at binding energies ~781.4 eV and ~796.5 eV are characteristic of Co²⁺ [24,41,42]. **Table 1** summarizes the Co³⁺/Co²⁺ ratios of the catalysts. **Figure 8** (b) shows the O 1s spectra of the samples. These are deconvoluted to 529.5-529.6 eV, 531.1-531.3 eV, and 532.6-532.9 eV which are ascribed to surface lattice oxygen, adsorbed oxygen species, and chemisorbed water respectively [24,41,42]. **Table 1** shows the O_{ads}/O_{latt} of the catalysts.



Figure 8. (a) Co 2p XPS spectra and (b) O 1s spectra of the Co₃O₄ catalysts.



Figure 9 *In situ* DRIFTS spectra of adsorbed 2-propanol on Co₃O₄-350 catalyst at different temperatures.

DRIFT spectra, carried out on Co₃O₄-350 is displayed in **Figure 9**. At 100 °C it is possible to notice a broad band at about 3263-3500 cm⁻¹, associated with the vibration of surface hydroxyl group [47],[48]. The peak at 2972 cm⁻¹ represents C-H stretching vibrations from the isopropyl H₃C group. The band at 1700 cm⁻¹ is due to the stretching of aliphatic C=O group [49],[50]. The bands at 1424,1463, can be attributed to asymmetric vibrations of non-coordinated carbonate species whereas the bands at 1565 cm⁻¹ can be attributed to vibration of carboxylate species [51],[52]. The bands at 1321 and 1372 cm⁻¹ were due to the splitting of the symmetric CH₃ scissors mode. Furthermore, the isopropyl group shows two characteristic bands at 1126 cm⁻¹ and 1156 cm⁻¹ due to its skeletal vibration [49]. The bands at 1230, 1260, and 1278 cm⁻¹ symmetric vibration of bidentate carbonate species [51],[53]. As far as temperatures from 150 °C to 350 °C are considered, bands for stretching vibrations of water and splitting of the symmetric CH₃ scissors (1372 cm⁻¹ and 1321 cm⁻¹) remain. Furthermore, bands characteristic of isopropyl

group at 1126 and 1156 cm⁻¹ persist with lower intensity. Moreover, bands for carbonate groups remain in similar intensity until 200 °C and start to increase after 200 °C. Another important feature is that the intensity of the band at 1700 cm⁻¹ significantly decreases at 150 °C whereas bands at 1650 and 1730 cm⁻¹ appears. In addition, the band at 1700 cm⁻¹ completely disappears at 200 °C while 1650 and 1730 cm⁻¹ remain. However, these three bands disappear at temperatures higher than 200 °C.

Discussion

Mesoporous cobalt oxide was used as a catalyst for the total oxidation of 2-propanol in this study. The synthesis of the cobalt oxide was done using the sol gel based inverse micelle method. Cobalt nitrate was used as the metal precursor and 1-butanol was used as the interface modifier and the solvent. Nitric acid hinders the condensation at lower pH. The surfactant used for the synthesis was P123 which forms inverse micelles which act as nanoreactors. Furthermore, uncontrolled aggregation is prevented by the individual surfactant molecules by acting as a barrier between metal oxo clusters. The nitrate ions form nitric oxides (NOx) by thermal decomposition. The formed NOx species adsorb on the metal oxo clusters to prevent uncontrolled condensation and they assist the oxidation of oxo clusters.[54] The heat treatment at 150 °C for 12 hours is necessary for the removal of the adsorbed NO_x and COO⁻ groups. The heat treatment at 250 °C produces the desired Co₃O₄ phase for catalysis. Calcination temperatures of 250 °C, 350 °C, and 450 °C were used to tune the structural and surface properties of the materials. The ramp rates and durations of the calcination seem to play an important role in tuning the properties of the materials synthesized by the inverse micelle method as emphasized by previous studies [55]. Interparticle voids of randomly packed monodispersed nanoparticles are responsible for the mesoporosity as evidenced by type IV adsorption isotherms [56]. The particle sizes were 4.6 ± 0.9 nm, 9.0 ± 1.8 nm, and 14.3 ± 1.9 nm for Co₃O₄- 250, Co_3O_4 -350, and Co_3O_4 -450 respectively indicating the increase of size with increasing temperature. The mesoporous materials synthesized show high surface areas (up to 121 m^2/g) compared to the commercial cobalt oxide $(3 \text{ m}^2/\text{g})$. Exposure of lattice oxygen to the catalytic surface is enhanced by the large surface areas and the nanoparticle nature of the materials.

The activity of the catalysts depends on several parameters such as surface area, porosity, active phase, surface oxygen species, oxidation states of metals, and reducibility [30]. The

unique pore structure of the mesoporous cobalt oxides is crucial for the high catalytic activity of these materials over bulk materials. The adsorption of reactants and diffusion of products is facilitated by mesopores. The largest pore volume is shown for the highest active Co₃O₄-350 catalyst which gives the lowest T₉₀ values both in higher and lower WHSV values. A catalyst with high surface area can expose more active sites for oxidation reactions, accounting for the higher activity of mesoporous materials over bulk cobalt oxide. Furthermore, this accounts for low mass diffusional distances in the catalyst giving high activity at low temperature.

The Mars-van-Krevelen mechanism is important for oxidation of VOCs [17], [57], [58]. Here, the organic molecule is oxidized by the lattice oxygens of the oxide, and these sites get reoxidized by gas phase oxygen. The presence of metals in different oxidation states which could be oxidized or reduced is important for this type of mechanism [16]. XPS can be used to identify the concentration of the difference valence states of elements. The peak area percentages of different cobalt oxidation states are given in **Table 1**. The Co³⁺/Co²⁺ ratios for catalysts calcined at 250 °C, 350 °C, and 450 °C were calculated to be 2.50, 2.63, and 2.00. This shows that Co_3O_4 -350 has the highest amount of Co^{3+} . Temperature programmed reduction experiments are useful for the evaluation of metal ion concentrations as reported in the literature[23],[24],[42] Figure 5 is considered, the intensity of the lowest reduction peak of Co₃O₄ 350 is As far as higher than other samples. This indicates the presence of higher amounts of Co^{3+} in Co_3O_4 -350 in conformity with XPS analysis. The higher amount of Co^{3+} may increase the anionic defect composition which results from larger surface areas and specific porous channels [27]. The catalytic activity is related to the higher concentration of Co^{3+} as detailed in the literature [23],[24],[30],[41],[59]. Co³⁺ cationic species assist the total oxidation of formaldehyde [27]. Furthermore, previous studies have found that in CO oxidation reactions, CO molecules interact preferably with surface Co^{3+} cations, which is supported experimentally and theoretically [30],[60]. Therefore, Co^{3+} cations may be acting as favorable sites for 2-propanol adsorption. Moreover, low temperature reducibility is a crucial factor for catalytic activity of materials [61]. The highest reducibility is shown by Co₃O₄-350. Therefore, catalytic activity is closely related to the low temperature reducibility. According to Figure 8 (b) the ratio of Oads to Olatt was calculated for the synthesized catalysts as shown in **Table 1**. The highest ratio is shown by the Co₃O₄-350 material. Higher values for O_{ads}/O_{latt} indicate a higher concentration surface active oxygen in the material which are responsible for higher activity in oxidation reactions [41].

In situ DRIFTS was used to confirm the intermediate species during 2-propanol oxidation on the surface of the catalyst from 100 °C to 350 °C. At 100 °C the catalyst surface accumulates peaks for the adsorbed species of 2-propanol such as surface hydroxyl and isopropyl CH₃ groups. Furthermore, the bands for carbonyl and adsorbed carbonate species are also seen at this temperature. As the reaction temperature is raised to 200 °C, the peaks for the isopropyl alcohol decreases in intensity. Moreover, a shift in the carbonyl peak is observed at 150 °C and 200 °C. The C=O vibration is rather sensitive to the physical state of the compound which may be the reason for the shift of this peak at higher temperature [49]. Furthermore, these peaks for carbonyls disappear after 200 °C and the peaks for carbonate species increases gradually. At temperatures lower than 200 °C, the catalysts surface facilitates the formation of carbonyl species, carbonate species and water. The carbonyl species may be desorbing the surface as acetone at low temperatures [43]. In addition, complete oxidation of the 2-propanol to carbon dioxide and water is confirmed by the gradual increase in the intensity of the adsorbed carbonate species and hydroxyl groups with the increasing reaction temperature.

The synthesized mesoporous cobalt oxides offer high tolerance to water vapor and carbon dioxide present in VOC streams. Only a slight decrease in activity is observed in catalytic activity probably due to the competitive adsorption of these molecules and blocking of active sites. The mesoporous cobalt oxide materials show a CoO phase together with the Co₃O₄ phase after the reaction (up to 340 °C). However, no phase change was observed for the catalysts after the reaction at 240 °C (stability tests). This implies that the catalysts start to undergo reduction at higher temperatures. This further confirms that at lower temperatures, lattice oxygens are used for the oxidation and are replenished by oxygen in the feed gas.

5. Conclusions

A soft template method was used to successfully synthesize mesoporous cobalt oxide materials and their activities were evaluated for low temperature 2-propanol oxidation. The synthesized materials exhibited impressive catalytic performance and excellent stability for 2-propanol oxidation. 2-propanol is oxidized to carbonyl species and carbonate species on the surface of the catalysts before being oxidized to carbon dioxide and water. Furthermore, the activity of materials was not significantly affected by water vapor or carbon dioxide in the stream. Catalysts which possess better low temperature reducibility, large pore volumes, higher Co^{3+}/Co^{2+}

amounts and higher number of surface-active oxygen species show better performance. The inverse micelle method which was utilized in this study is promising for the synthesis of mesoporous cobalt oxide with high catalytic activity. This work provides a novel method for developing noble metal free catalysts to eliminate VOCs at lower temperature.

Conflict of interest

The authors declare no competing financial interest.

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References

- C. He, J. Cheng, X. Zhang, M. Douthwaite, S. Pattisson, Z. Hao, Chem. Rev. 119 (2019) 4471– 4568.
- [2] O.S.G.P. Soares, A.M. Fonseca, P. Parpot, J.J.M. Órfão, M.F.R. Pereira, I.C. Neves, ChemCatChem 10 (2018) 3754–3760.
- [3] M.S. Kamal, S.A. Razzak, M.M. Hossain, Atmos. Environ. 140 (2016) 117–134.
- [4] F.N. Aguero, B.P. Barbero, L. Gambaro, L.E. Cadús, Appl. Catal. B: Environ. 91 (2009) 108–112.
- [5] B. Solsona, T. García, R. Sanchis, M.D. Soriano, M. Moreno, E. Rodríguez-castellón, S. Agouram, Chem. Eng. J. 290 (2016) 273–281.
- [6] Z. Wang, Y. Qin, F. Pan, Z. Li, W. Zhang, F. Wu, D. Chen, W. Wen, J. Li, Ind. Eng. Chem. Res. 57 (2018) 7374–7382.
- [7] A. Aboukaïs, M. Skaf, S. Hany, R. Cousin, S. Aouad, M. Labaki, E. Abi-Aad, Mater. Chem. Phys. 177 (2016) 570–576.
- [8] Z. Zhang, X. Yan, F. Gao, P. Thai, H. Wang, D. Chen, L. Zhou, D. Gong, Q. Li, L. Morawska, B. Wang, Environ. Pollut. 238 (2018) 452–461.
- [9] B. Huang, C. Lei, C. Wei, G. Zeng, Environ. Int. 71 (2014) 118–138.
- [10] D.R. Gentner, R. a Harley, A.M. Miller, A.H. Goldstein, Environ. Sci. Technol. 43 (2009) 4247– 4252.
- [11] R. Wang, J. Li, Environ. Sci. Technol. 44 (2010) 4282–4287.
- [12] S. Scirè, L. Francesca, Appl Catal. B, Environ. 125 (2012) 222–246.
- [13] Y. Dumanoglu, M. Kara, H. Altiok, M. Odabasi, T. Elbir, A. Bayram, Atmos. Environ. 98 (2014) 168–178.
- [14] H. Huang, Y. Xu, Q. Feng, D.Y.C. Leung, Catal. Sci. Technol. 5 (2015) 2649–2669.
- [15] W.P. Stege, L.E. Cadús, B.P. Barbero, Catal. Today 172 (2011) 53–57.
- [16] S.A. Hosseini, A. Niaei, D. Salari, S.R. Nabavi, Ceram. Int. 38 (2012) 1655–1661.
- [17] S.A. Hosseini, D. Salari, A. Niaei, F. Deganello, G. Pantaleo, P. Hojati, J. Environ. Sci. Heal. Part A 46 (2011) 291–297.
- [18] L. Pahalagedara, D.A. Kriz, N. Wasalathanthri, C. Weerakkody, Y. Meng, S. Dissanayake, M. Pahalagedara, Z. Luo, S.L. Suib, P. Nandi, R.J. Meyer, Appl. Catal. B Environ. 204 (2017) 411–420.
- [19] H.C. Genuino, S. Dharmarathna, E.C. Njagi, M.C. Mei, S.L. Suib, J. Phys. Chem. C 116 (2012) 12066–12078.

- [20] M. Konsolakis, S.A.C. Carabineiro, P.B. Tavares, J.L. Figueiredo, J. Hazard. Mater. 261 (2013) 512–521.
- [21] H. Huang, D.Y.C. Leung, J. Catal. 280 (2011) 60–67.
- [22] B. de Rivas, R. López-Fonseca, C. Jiménez-González, J.I. Gutiérrez-Ortiz, J. Catal. 281 (2011) 88–97.
- [23] X. Ma, X. Yu, X. Yang, M. Lin, M. Ge, ChemCatChem 11 (2019) 1214–1221.
- [24] Q. Ren, S. Mo, R. Peng, Z. Feng, M. Zhang, L. Chen, M. Fu, J. Wu, D. Ye, J. Mater. Chem. A 6 (2018) 498–509.
- [25] L. Francesca Liotta, H. Wu, ab Giuseppe Pantaleo, A. Maria Venezia, Catal. Sci. Technol 3 (2013) 3073–3378.
- [26] Y. Li, W. Shen, Chem Soc Rev. 43 (2014) 1543-1574.
- [27] B. Bai, H. Arandiyan, J. Li, Appl Catal. B: Environ. 142–143 (2013) 677–683.
- [28] C.Y. Ma, Z. Mu, J.J. Li, Y.G. Jin, J. Cheng, G.Q. Lu, Z.P. Hao, S.Z. Qiao, J. Am. Chem. Soc. 132 (2010) 2608–2613.
- [29] Y. Yu, T. Takei, H. Ohashi, H. He, X. Zhang, M. Haruta, J. Catal. 267 (2009) 121–128.
- [30] X. Xie, Y. Li, Z. Liu, M. Haruta, W. Shen, Nature 458 (2009) 746–749.
- [31] Y. Zheng, Y. Liu, H. Zhou, W. Huang, Z. Pu, J. Alloys Compd. 734 (2018) 112–120.
- [32] Z. Fei, S. He, L. Li, W. Ji, C.T. Au, Chem. Commun. 48 (2012) 853-855.
- [33] W.J. Xue, Y.F. Wang, P. Li, Z.-T. Liu, Z.P. Hao, C.Y. Ma, Catal. Commun. 12 (2011) 1265–1268.
- [34] B. Xiao, K. Zhao, L. Zhang, T. Cai, X. Zhang, Z. Wang, J. Yuan, L. Yang, P. Gao, D. He, Catal. Commun. 116 (2018) 1–4.
- [35] W. Tang, W. Xiao, S. Wang, Z. Ren, J. Ding, P.X. Gao, Appl. Catal. B: Environ. 226 (2018) 585– 595.
- [36] Y. Du, Q. Meng, J. Wang, J. Yan, H. Fan, Y. Liu, H. Dai, Microporous Mesoporous Mater. 162 (2012) 199–206.
- [37] B. De Rivas, R. López-Fonseca, C. Jiménez-González, J.I. Gutiérrez-Ortiz, J. Catal. 281 (2011) 88–97.
- [38] S.A. Hosseini, M.C. Alvarez-Galvan, J.L.G. Fierro, A. Niaei, D. Salari, Ceram. Int. 39 (2013) 9253–9261.
- [39] N.D. Wasalathanthri, T.M. Santamaria, D.A. Kriz, S.L. Dissanayake, C. Kuo, S. Biswas, S.L. Suib, Applied Catal. B: Environ. 201 (2017) 543–551.
- [40] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Pure Appl. Chem. 87 (2015) 1051–1069.
- [41] Q. Ren, Z. Feng, S. Mo, C. Huang, S. Li, W. Zhang, L. Chen, M. Fu, J. Wu, D. Ye, Catal. Today

332 (2019) 160-167.

- [42] G. Li, C. Zhang, Z. Wang, H. Huang, H. Peng, X. Li, Appl. Catal. A Gen. 550 (2018) 67–76.
- [43] P. Lakshmanan, L. Delannoy, C. Louis, N. Bion, J.M. Tatibouët, Catal. Sci. Technol. 3 (2013) 2918–2925.
- [44] N.D. Wasalathanthri, A.S. Poyraz, S. Biswas, Y. Meng, C. Kuo, D.A. Kriz, S.L. Suib, J. Phys. Chem. C 119 (2015) 1473–1482.
- [45] Z. Ren, Z. Wu, W. Song, W. Xiao, Y. Guo, J. Ding, S.L. Suib, P.X. Gao, Appl. Catal. B: Environ. 180 (2016) 150–160.
- [46] S.Y. Chen, W. Song, H.J. Lin, S. Wang, S. Biswas, M. Mollahosseini, C.H. Kuo, P.X. Gao, S.L. Suib, ACS Appl. Mater. Interfaces 8 (2016) 7834–7842.
- [47] R. Fiorenza, M. Bellardita, L. Palmisano, S. Scirè, 415 (2016) 56–64.
- [48] J. Wang, G. Zhang, zhang peng, J. Mater. Chem. A 5 (2017) 5719–5725.
- [49] H.A. Szymanski, IR, Theory and Practice of Infrared Spectroscopy, Plenum Press, New York, 1964.
- [50] W. Qian, H. Wang, Y. Xu, X. Yang, G. Zhai, H. Zhang, H. Ma, Q. Sun, W. Ying, Ind. Eng. Chem. Res. 58 (2019) 6288–6297.
- [51] A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, John Wiley and Sons, Chister New York Brisbane Toronto Singapore, 1990.
- [52] M.J. Pollard, B.A. Weinstock, T.E. Bitterwolf, P.R. Griffiths, 254 (2008) 218–225.
- [53] J. Wang, J. Li, C. Jiang, P. Zhou, P. Zhang, J. Yu, Appl. Catal. B Environ. 204 (2017) 147–155.
- [54] A.S. Poyraz, C.-H. Kuo, S. Biswas, C.K. King'ondu, S.L. Suib, Nat. Commun. 4 (2013) 1–10.
- [55] C.J. Guild, D. Vovchok, D.A. Kriz, A. Bruix, B. Hammer, J. Llorca, W. Xu, A. El-Sawy, S. Biswas, J.A. Rodriguez, S.D. Senanayake, S.L. Suib, ChemCatChem 9 (2017) 1373–1377.
- [56] A.S. Poyraz, W. Song, D. Kriz, C. Kuo, M.S. Seraji, S.L. Suib, ACS Appl. Mater. Interfaces 6 (2014) 10986–10991.
- [57] A.Z. Abdullah, M.Z. Abu Bakar, S. Bhatia, Ind. Eng. Chem. Res. 42 (2003) 6059–6067.
- [58] E.R. Stobbe, B.A. de Boer, J.W. Geus, Catal. Today 47 (1999) 161–167.
- [59] Q. Liu, L.C. Wang, M. Chen, Y. Cao, H.Y. He, K.N. Fan, J. Catal. 263 (2009) 104–113.
- [60] A. Grillo, Federico Natile, Marta Maria Glisenti, Appl. Catal. B: Environ. 48 (2004) 267–274.
- [61] Y. Xia, H. Dai, H. Jiang, L. Zhang, CATCOM 11 (2010) 1171–1175.