



Synthesis, characterization and *in situ* DRIFTS during the CO₂ hydrogenation reaction over supported cobalt catalysts

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ABSTRACT

Several supported cobalt catalysts were synthesized, characterized, and studied by *in situ* diffuse reflectance Fourier-transformed infrared (DRIFT) spectroscopy during the CO₂ hydrogenation reaction. The calcined supported cobalt catalysts possessed Co₃O₄ on the different supports. The alumina supported cobalt catalysts formed increasing amounts of cobalt aluminate at calcination temperatures greater than 973 K. For magnesia supported cobalt catalyst a solid solution was observed at 1173 K. The most active alumina supported cobalt catalyst is formed upon reduction of the freshly calcined samples at 823 K in hydrogen. During hydrogen-reduction the supported Co₃O₄ phase is converted to CoO and cobalt metal at intermediate temperatures and to cobalt metal at 823 K. Reduced alumina supported cobalt is able to adsorb CO₂ as carbonate species; however, silica supported cobalt does not show carbonate species. For magnesia supported cobalt the presence of adsorbed CO₂ is not conclusive. The supported cobalt catalysts are active for the CO₂ hydrogenation reaction and the conversion depends on the reduction temperature, loading, and support. During reaction adsorbed CO is present on the supported cobalt metal irrespective of the support, whereas, surface formate species is only observed on alumina and magnesia supported cobalt catalysts. The carbonate and formate species does not correlate with the CO₂ conversion and appears to be formed on the metal–support interface. Thus, the reduction temperature, loading, and support are important factors while designing the supported cobalt catalysts.

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1. Introduction

Supported cobalt systems are important catalysts for many important chemical processes, especially those involving hydrogen. For example, supported cobalt is an important component of the catalysts for the hydrodesulfurization (HDS) of crude [1,2], and for the reaction of carbon monoxide and hydrogen to form higher hydrocarbons [3,4]. There are also patent disclosures for using supported cobalt catalyst for the reductive amination of ethanol [6]. Furthermore, there is an interest for using supported cobalt catalysts for the steam reforming of ethanol and methane decomposition [7–9].

Several supports have been considered for the synthesis of supported cobalt catalysts [10]. The supports include: alumina, silica, magnesia, titania, and zirconia. The interaction of cobalt with the support phase has also been studied and it has been observed that some of the factors that affect the nature of the interactions are: preparation method [4], reduction temperature [11,12], metal loading [10] and the support [4,10]. For example, in the alumina supported cobalt catalysts the formation of cobalt metal (Co), cobalt

oxides (Co₃O₄ and CoO), cobalt aluminate (CoAl₂O₄) or a surface CoAl₂O₄ has been proposed [4,5,13–16]. The nature of the cobalt phase in supported catalysts has been studied by a variety of characterization techniques. Some of the characterization techniques considered to better understand the cobalt phase in supported cobalt catalysts are: X-ray diffraction (XRD) [4,13–16], temperature programmed reduction and oxidation (TPR and TPO) [4,14,15], Raman spectroscopy [4,15,16], and UV–vis spectroscopy [4,14,16]. Several other characterization techniques have also been considered to understand this important catalytic material [4,14,16].

The present study aims to address some of the factors that affect the supported cobalt catalysts, such as the reduction temperature, metal loading, and the support, by synthesizing several series of supported cobalt catalysts, and characterizing these catalysts using X-ray diffraction (XRD) and UV–vis–NIR spectroscopy. To understand the effect of these factors on the reactivity of the supported cobalt catalysts the carbon dioxide (CO₂) hydrogenation reaction was considered as a probe reaction. This CO₂ hydrogenation reaction over the supported cobalt catalysts were specifically studied by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy with the simultaneous collection of the reaction data. It is expected that utilizing these various techniques and the probe reaction a better understanding of the supported cobalt catalysts will be available.

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2. Experimental

2.1. Material synthesis

A series of supported cobalt catalysts of different metal loadings (5, 10, 15, and 20 wt% cobalt) were prepared by the incipient wetness impregnation (IWI) method. The precursor and supports used were cobalt (II) nitrate hexahydrate (Merck, 98%), alumina (Sasol), magnesia (Merck, 98.6%), and silica (AEROSIL-200). Initially, the supports were pre-treated by incipient amounts of double-distilled water and after a series of drying and heating steps, as given below, were finally calcined at 773 K for 9 h. In the IWI method the precursor, cobalt (II) nitrate hexahydrate, was dissolved with an incipient wetness volume of water to form a solution. This precursor solution was added drop wise to a measured amount of pretreated support and the two were thoroughly mixed. The impregnated support was then kept overnight in a desiccator. The dried samples were further dried in an oven at 383 K for 6 h and stage-wise calcined at various temperatures and finally at 773 K for 9 h. The samples were denoted as $x\text{CoAl}$, $x\text{CoMg}$, or $x\text{CoSi}$, where x is the wt% of cobalt metal in the sample containing the support: alumina (Al), magnesia (Mg), or silica (Si).

2.2. Characterization studies

The surface areas of all the samples were determined by nitrogen adsorption using the single point BET equation. The adsorption gas was a 30% N_2 –He gas mixture and a SMART SORB 92/93 BET Surface area analyzer was used. For the surface area measurement 50–60 mg of the samples were taken and degassed at 423 K before the measurement.

The XRD pattern of all the samples were obtained in the range of 15–90° with a scanning range of 3°/min on an X'Pert Powder Diffractometer using $\text{Cu K}\alpha$ irradiation ($\lambda = 1.541841 \text{ \AA}$). The metal particle sizes were calculated using the X'Pert High Score Plus software available with the equipment.

The reducibility of the prepared catalysts was also studied in a UV–vis–NIR spectrophotometer (Cary 5000) equipped with a diffuse reflectance accessory (Harrick Scientific). All spectra were collected under ambient conditions with BaSO_4 as the reference.

2.3. DRIFT studies

The DRIFT spectra of the supports and supported cobalt catalysts were recorded on a BRUKER TENSOR 27 FTIR spectrometer attached with a Praying Mantis, diffuse reflectance accessory and a high temperature reaction chamber (HARRICK HVC-DRP-2) equipped with ZnSe windows. To obtain the DRIFT spectra, a measured amount of powder sample was loaded into the sample cup of the high temperature reaction chamber. The reaction cell was heated by an automatic temperature controller module (HARRICK ATC-024-2). The spectra were collected at a resolution rate of 4 cm^{-1} . Using the DRIFT setup two types of studies were carried out: CO_2 adsorption and CO_2 hydrogenation reaction studies.

2.3.1. Carbon dioxide adsorption

Carbon dioxide adsorption studies were performed over the Al_2O_3 , MgO, and SiO_2 supports and $x\text{CoAl}$, $x\text{CoMg}$, and $x\text{CoSi}$ catalysts using the DRIFT setup described above. Samples of 60–100 mg were loaded in the sample cup and were reduced at 823 K for 1/2 h in a stream of hydrogen flowing at 11.6 ml/min. After reduction the reaction cell was purged by a helium stream for 1 h and then with helium flowing the temperature was reduced to 533 K. After helium purge pure carbon dioxide was introduced into the reaction chamber. The adsorption study was carried at 533 K using carbon dioxide flowing at 2 ml/min. The flow rate of each gas stream was adjusted

Table 1
Surface area of the catalysts calcined at 773 K.

Samples	BET area (m^2/g)	Samples	BET area (m^2/g)
Al_2O_3	200	SiO_2	192
5CoAl	162	15CoSi	167
10CoAl	156	MgO	28
15CoAl	145	15CoMg	52
20CoAl	120		

by separate mass flow controllers (Bronkhorst) and the gases were passed through the catalyst bed in a down-flow mode. Depending on the sample the spectra were recorded against dehydrated $x\text{CoAl}$, $x\text{CoMg}$, or $x\text{CoSi}$ in a He background.

2.3.2. Carbon dioxide hydrogenation reaction

Carbon dioxide hydrogenation reaction studies were also carried out in the same DRIFT set up as described above. In the present study the supports and $x\text{CoAl}$, $x\text{CoMg}$, and $x\text{CoSi}$ catalysts were considered. Prior to the reaction the samples were reduced in a fixed bed reactor in a stream of hydrogen (H_2) flowing at 40 ml/min for 4 h at various temperatures. To study the effect of reduction temperature the reduced catalyst was loaded into the reaction chamber and again reduced at various temperatures ranging from 623 to 823 K for 1 h. The highest *in situ* reduction temperature was 823 K due to the constraints of the reaction chamber. After *in situ* reduction the temperature of the reaction chamber was reduced to the reaction temperature. The reaction temperature was kept constant at 533 K. A total inlet reactants flow rate of H_2 and CO_2 was maintained at 13.5 ml/min with H_2 to CO_2 molar ratio of 6.0:1.0, which was maintained by separate mass flow controllers (Bronkhorst). As above, the gases were passed through the catalyst bed in a down-flow mode. The IR spectra were recorded against a background of dehydrated $x\text{CoAl}$, $x\text{CoMg}$, or $x\text{CoSi}$ in a H_2 environment. Gas samples were collected in a gas sampling chamber connected to the exit of the reaction cell. Samples from the sampling chamber were injected into a gas chromatograph (GC) (AIMIL) equipped with methanizer and a FID detector. A 3 m Carbosphere column was used in the GC for separation of the components. Blank experiments were also conducted under identical reaction conditions with the flow of reactants, H_2 and CO_2 , to ensure no contribution of homogeneous reaction in the reactor occurred under the present conditions.

For the 15CoAl, 15CoMg, and 15CoSi catalysts two sets of experiments involving the CO_2 hydrogenation reaction were carried out. In the first set of experiments the sample cup was filled with known amounts of catalysts and the DRIFT spectra and reaction data were obtained. It was observed that the amount of catalyst was significantly different. In the second set of experiments the catalyst amount was kept constant and equal to the sample with the least density, 15CoSi. Thus, the amounts of 15CoAl and 15CoMg did not fill the sample cup.

3. Results and discussion

3.1. Surface area analysis

The surface areas of the freshly calcined catalysts were measured and the results are tabulated in Table 1. From Table 1 it is observed that the surface area decreases with addition of cobalt for the alumina and silica supported catalysts. Furthermore, for the alumina supported catalysts the surface area continuously decreases with the increasing addition of cobalt. For the magnesia supported cobalt catalyst, however, the surface area increases. Such increases in surface area have been previously reported [17]. A decrease in surface area with metal loading for the Al_2O_3 and SiO_2 supported

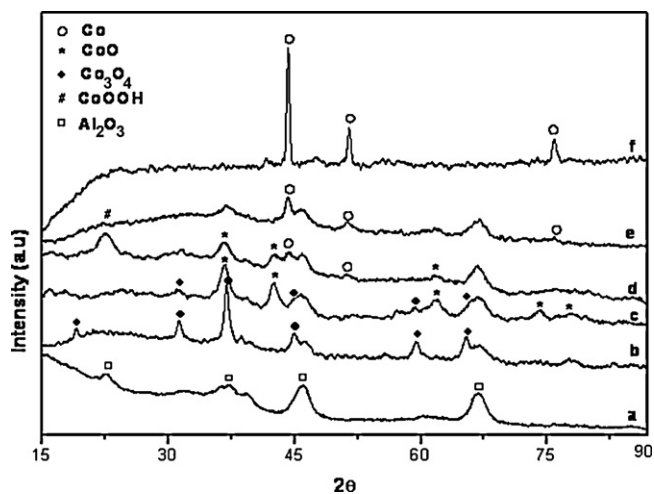


Fig. 1. XRD patterns of (a) Al_2O_3 , (b) 15CoAl calcined at 773 K; and 15CoAl reduced at (c) 623 K, (d) 723 K, (e) 823 K, and (f) bulk Co_3O_4 reduced at 823 K.

cobalt catalysts has been observed previously [19] and is usually associated with changes in micropores and the difference of atomic weight of Co_3O_4 and the supports.

3.2. X-ray diffraction pattern study

The XRD patterns of the 15CoAl sample reduced in hydrogen at 623–823 K were obtained and are shown in Fig. 1. The XRD patterns were compared with the freshly calcined supported cobalt samples and unsupported bulk cobalt metal synthesized by the reduction of bulk Co_3O_4 at 823 K. It appears that part of the Co_3O_4 phase present in the 15 wt% cobalt supported on alumina catalysts is reduced to CoO phase during reduction at 623 K. The reduction is, however, incomplete since Co_3O_4 features are still observed. The presence of cobalt metal at a reduction temperature of 623 K is not evident in the XRD pattern, which may be due to the inability of XRD to detect small crystals [4]. The absence of cobalt metal features in the XRD pattern does not discount the presence of cobalt metal at a reduction temperature of 623 K on the 15 wt% cobalt supported catalyst. With increasing reduction temperature it appears that the CoO phase is reduced and Co metal features are clearly observed at 723 K. Furthermore, at a reduction temperature of 723 K, a band was observed at 22.5° , which has been attributed to cobalt oxide hydroxide (CoOOH) formation [14,24]. At a reduction temperature of 823 K, cobalt metal appears to be the only cobalt phase present. A previous study suggests that a reduction temperature of 723 K is required for the reduction of most of the Co_3O_4 phase to Co metal [23]. The present study reveals that the complete reduction of the alumina supported Co_3O_4 phase requires a temperature of 823 K.

The formation and reduction of the different cobalt oxide phases with increasing reduction temperature suggests that the reduction of Co_3O_4 to Co metal occurs via the formation of CoO/CoOOH phase. Only Co_3O_4 phase is present in the sample calcined at 773 K; Co_3O_4 , CoO, CoOOH and possibly Co metal co-exists at the reduction temperature at 723 K and only Co metal is present at 823 K. Using XRD the presence of CoAl_2O_4 is not evident, which may be due to the considerable overlap of the features due to Co_3O_4 and CoAl_2O_4 . Thus, based on the XRD patterns a reduction temperature of 823 K is necessary to reduce Co_3O_4 and CoO to Co metal.

The XRD patterns of the $x\text{CoAl}$ catalysts reduced at 823 K are shown in Fig. 2. Analysis of Fig. 2 reveals that with increasing cobalt loading the crystalline phase of cobalt metal gradually increases. XRD features of cobalt oxides, cobalt oxide hydroxide and CoAl_2O_4 are not evident for the series of $x\text{CoAl}$ catalysts reduced at 823 K in H_2 .

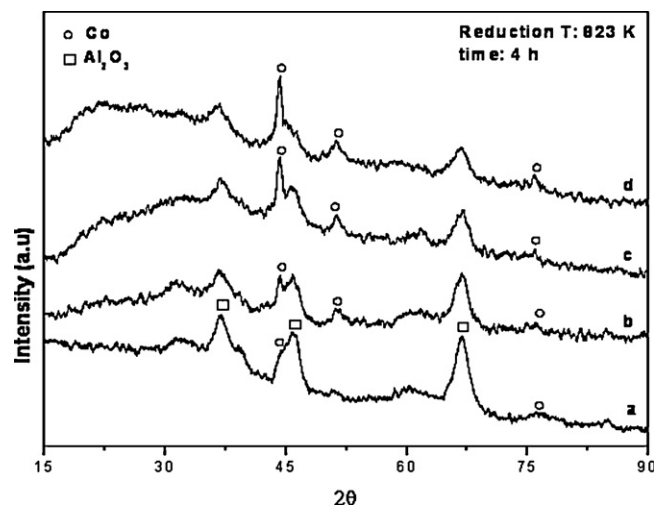


Fig. 2. XRD patterns of $x\text{CoAl}$ ($x=5-20$ wt%) reduced at 823 K; (a) 5CoAl, (b) 10CoAl, (c) 15CoAl, and (d) 20CoAl.

The support effect for 15 wt% cobalt loading samples, 15CoAl, 15CoSi, and 15CoMg, was studied and the XRD patterns of the samples calcined at 773 K revealed features of the supports and Co_3O_4 . The Co_3O_4 features in the XRD patterns were distinct for the 15CoSi and 15CoAl samples and of low intensity for the 15CoMg sample. As noted above for the alumina supported cobalt catalysts and from the XRD patterns of the silica supported cobalt catalysts, it appears that only Co_3O_4 is formed on the surface of alumina and silica at a calcination temperature of 773 K. For the magnesia supported cobalt oxide catalysts, however, the situation is more involved since it is known that cobalt can interact with magnesia to form different phases even at 773 K [17,18]. It has been suggested that at these temperatures cobalt oxide interacts with magnesia to form MgCo_2O_4 , which may be a reason for the low intensity of the Co_3O_4 features in the XRD patterns of 15CoMg.

The XRD patterns of the 15CoAl, 15CoSi, and 15CoMg samples reduced at 823 K are shown in Fig. 3. For the 15CoAl and 15CoSi samples reduced at 823 K, distinct features of Co metal were observed. Furthermore, a small feature associated with CoO was observed for the 15CoSi sample reduced at 823 K, suggesting incomplete reduction of this sample. For the 15CoMg sample, the presence of cobalt metal was not evident, which may be due to

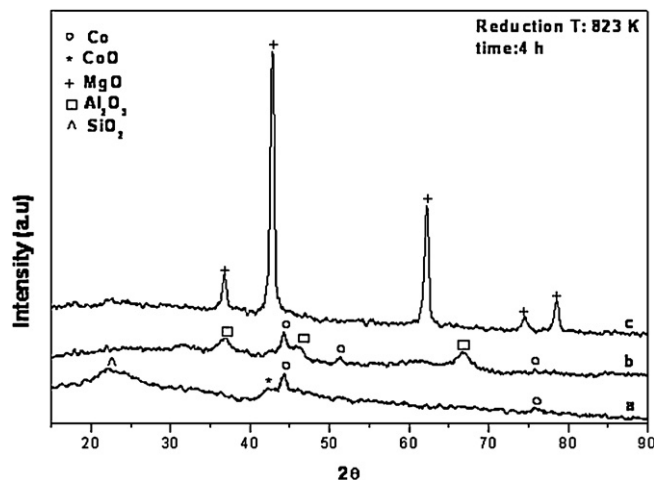


Fig. 3. XRD patterns of 15 wt% Co catalysts on various supports reduced at 823 K (a) 15CoSi, (b) 15CoAl, and (c) 15CoMg.

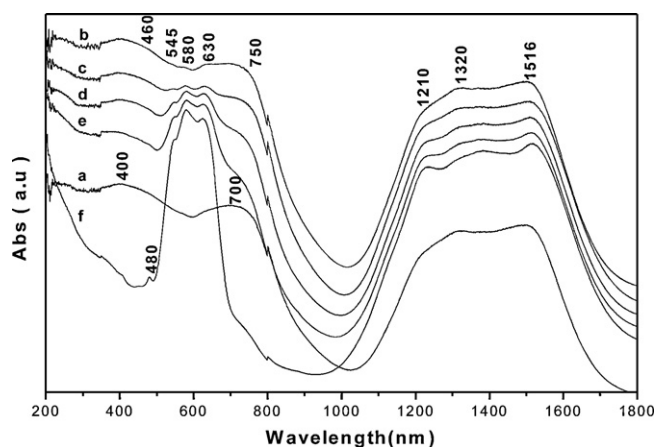


Fig. 4. UV-vis-NIR spectra of 15CoAl calcined at (a) 773 K, (b) 973 K, (c) 1023 K, (d) 1073 K, (e) 1123 K, and (f) 1173 K.

the small size of the cobalt metal and/or highly dispersed cobalt species on magnesia [18].

The mean sizes of the cobalt metal crystallites were determined. A 2θ value of 44.16 of the cobalt metal was considered. Silicon was considered as the standard. For the 15CoAl catalyst, with increasing reduction temperature the mean crystallite size increases and the reduction of cobalt oxide is more. For the series of alumina supported cobalt catalyst at particular reduction temperature of 823 K (where it is observed that no cobalt oxide phase is present), the mean crystal size increases with increasing cobalt loading. Thus, with increasing reduction temperature at a particular loading and with increasing loading at the particular reduction temperature the amount of surface cobalt metal sites per gram catalyst increases.

For the 15CoMg catalyst reduced at 823 K, cobalt metal is not observed by XRD. Thus, no conclusive statement can be made regarding the cobalt metal site for this sample. For the 15CoAl and 15CoSi catalysts reduced at 823 K, analysis of the XRD pattern reveals that the mean crystal size is smaller for the 15CoSi than the 15CoAl catalyst. For the 15CoSi sample, however, complete reduction of the cobalt oxide did not occur since CoO is still observed in the XRD pattern (see Fig. 3). Thus, it appears that for the 15CoSi catalyst the amount of surface cobalt metal per gram catalyst is smaller than that observed for the 15CoAl catalyst.

3.3. UV-vis-NIR spectra analysis

The 15CoAl catalysts calcined at different temperature from 773 to 1173 K was studied by UV-vis-NIR spectroscopy and the spectra obtained under ambient conditions are shown in Fig. 4. The freshly calcined 15CoAl at 773 K possesses distinct bands at 400 and 700 nm indicating the presence of octahedral Co^{3+} ion similarly to that in Co_3O_4 [22] and a shoulder at 460 nm, which has been assigned to Co^{2+} in an octahedral environment [20]. Additional bands were observed in the NIR region at 1210, 1320, and 1516 nm. These three additional bands are assigned to the tetrahedral Co^{2+} ions in Co_3O_4 [16]. At calcination temperatures of 973 K new bands were observed in UV-vis spectrum. The new bands at 545, 580, and 630 nm and at 1230, 1380, and 1516 nm are due to the cobalt aluminate (CoAl_2O_4) species, where cobalt is present as a Co^{2+} species in a tetrahedral environment [16]. The CoAl_2O_4 formation increases with increasing calcination temperature up to 1173 K. During the phase transformation of octahedral Co^{3+} to tetrahedral Co^{2+} species new bands were observed at 460 and 750 nm. These bands correspond to Co^{2+} in an octahedral environment [16,20]. A new band was observed at 480 nm during the calcination at 1173 K.

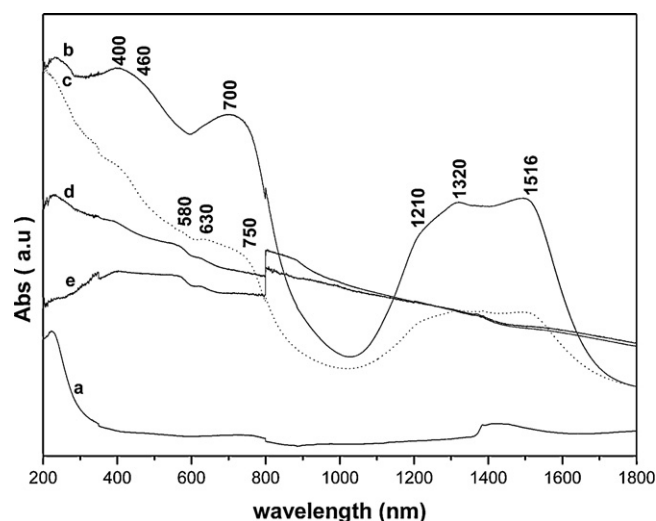


Fig. 5. UV-vis-NIR spectra of (a) Al_2O_3 , (b) 15CoAl calcined at 773 K; and 15CoAl reduced at (c) 623 K, (d) 723 K, and (e) 823 K.

The assignment of this band is still not clear and may be due to cobalt aluminate.

As a function of calcination temperature the 15CoMg sample reveals the presence of bands at 400, 700, 1210, 1320, and 1516 nm at 773 K. The intensity of these bands were, however, lower than those observed for the 15CoAl and 15CoSi samples calcined at the same temperature. Considering the lower intensity of the Co_3O_4 features in the XRD pattern for the 15CoMg sample, it appears that the amount of Co_3O_4 present in this sample is smaller. As suggested before the remaining cobalt may be present as MgCo_2O_4 [17]. For the 15CoMg sample calcined at 1173 K, new bands at 290, 520, and 1200 nm were observed. It appears that the 290, 520, and 1200 nm bands correspond to the formation of a solid solution of cobalt in magnesia, which has been proposed earlier [17]. Thus, the calcination temperature effects for 15CoMg suggest that part of the cobalt in the 15CoMg catalyst is present as Co_3O_4 at a calcination temperature of 773 K and only a cobalt-magnesia solid solution is formed at 1173 K.

As a function of calcination temperature, the 15CoSi sample reveals bands due to Co_3O_4 , which do not change when calcined up to or 1073 K. Consequently, the silica support does not interact strongly with the cobalt phase. The interaction of the cobalt phase with the alumina and magnesia support is more significant since the formation of CoAl_2O_4 occurs at 973 K and above; formation of MgCo_2O_4 occurs even at 773 K and cobalt-magnesia solid solution occurs at 1173 K.

The 15CoAl catalyst pre-calcined at 773 K and reduced at different temperatures was also studied by UV-vis-NIR spectroscopy and the spectra are shown in Fig. 5. The Al_2O_3 support is included as a reference. The 400, 460 (shoulder), and 700 nm bands observed in the freshly calcined sample gradually disappear with increasing reduction temperature from 623 to 823 K. With the decrease in intensity of these three bands new bands at 630 and 750 nm were observed. Further reduction decreases the intensity of the 750 nm band and bands at 580 and 630 nm were observed. Bands at 542, 584, and 625 nm have been attributed to Co^{2+} in a tetrahedral environment [25], however, the absence of the band at 542 nm makes this assignment debatable. UV-vis-NIR spectra of several alumina supported metals that have been reduced under similar conditions also show the presence of this band. Furthermore, the spectra of the $x\text{CoAl}$, 15CoMg, and 15CoSi catalysts reduced at 823 K were also obtained and the spectra reveal the presence of the 580 and 630 nm bands. Thus, the assignment of the 580 and 630 nm bands

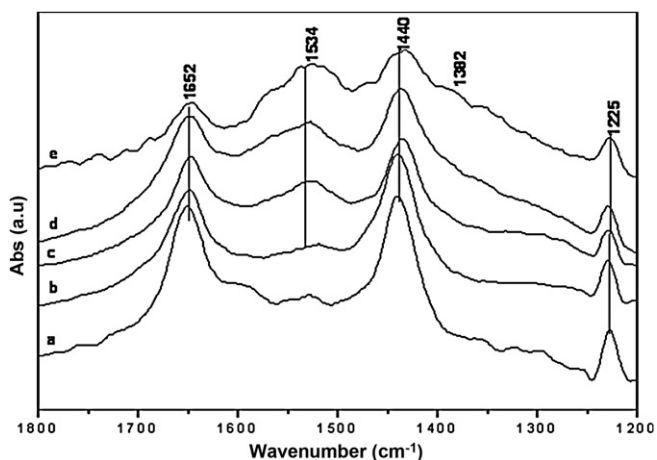


Fig. 6. *In situ* DRIFT spectra of CO₂ adsorption at 533 K over (a) Al₂O₃ and (b) 15CoAl calcined at 773 K; and reduced in hydrogen at (c) 623 K, (d) 723 K, and (e) 823 K.

at this point is unclear and additional studies are required for its assignment.

3.4. DRIFT studies

Two types of DRIFT studies were considered: carbon dioxide adsorption and carbon dioxide hydrogenation reaction. In all the DRIFT spectra IR bands due to gas phase CO₂ are observed.

3.4.1. Carbon dioxide adsorption

3.4.1.1. Effect of catalysts reduction temperature. The adsorption of carbon dioxide was studied as a function of the catalyst reduction temperature for the 15CoAl catalyst, which was pre-calcined at 773 K. The adsorption of CO₂ was performed at 533 K and the results are shown in Fig. 6. The adsorption of CO₂ on the Al₂O₃ support and the freshly calcined 15CoAl sample is included for reference. Carbon dioxide adsorption on Al₂O₃ gives rise to IR bands at 1225, 1440, and 1652 cm⁻¹, which are assigned to bicarbonate species [21]. Weak bands at 1534 and 1600 cm⁻¹ were also observed. The bicarbonate bands were also observed for the freshly calcined 15CoAl sample, though these bands are of lower intensity. For the reduced 15CoAl catalysts an additional band at 1534 cm⁻¹ and a broad shoulder at ~1382 cm⁻¹ were observed. These two bands increase in intensity with increase in reduction temperature and are assigned to carbonate species [21]. These results suggest that the carbonate formation is associated with the cobalt metal that are increasingly formed from the remaining cobalt oxides during the reduction of the catalysts at higher temperatures.

3.4.1.2. Effect of metal loading. The formation of carbonate and bi-carbonate species during CO₂ adsorption over the series of xCoAl catalysts reduced at 823 K was observed and the spectra are shown in Fig. 7. The carbonate species gradually increases with increasing cobalt loading up to 15 wt% of cobalt metal. Simultaneously, the bi-carbonate species gradually decreases. Above 15 wt% cobalt loading, the carbonate and bi-carbonate formations both decrease. It appears that up to 15 wt% cobalt loading the alumina support is progressively covered and above this loading only a small part of the support is available for CO₂ adsorption. Furthermore, it appears that up to 15 wt% cobalt loading the cobalt metal is available for CO₂ adsorption and above this loading the amount of cobalt metal available for CO₂ adsorption decreases.

3.4.1.3. Effect of support. The adsorption of CO₂ over the reduced 15 wt% cobalt on the Al₂O₃ and MgO supports were also studied and the DRIFT spectra are shown in Fig. 8. The adsorption of CO₂

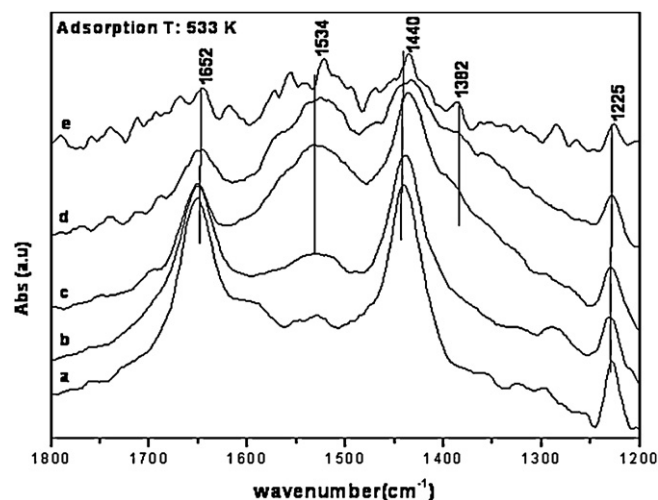


Fig. 7. *In situ* DRIFT spectra of CO₂ adsorption at 533 K over xCoAl ($x=5-20$ wt%) catalysts reduced at 823 K and Al₂O₃; (a) Al₂O₃, (b) 5CoAl, (c) 10CoAl, (d) 15CoAl, and (e) 20CoAl.

over the Al₂O₃, SiO₂, and MgO supports were also studied. For SiO₂ and 15CoSi, no CO₂ adsorption bands were observed and the spectra are not shown for brevity. For the 15CoAl and 15CoMg catalysts, however, distinct carbonate and bi-carbonate species were observed. The presence of carbonate and bicarbonate species over the 15CoAl catalyst was discussed above. For the 15CoMg catalyst, the magnesia support itself strongly adsorbs CO₂ as: bi-carbonate species, with IR bands at 1220, 1424, and 1655 cm⁻¹; bi-dentate carbonate species, with IR bands at 1308 and 1671 cm⁻¹; and as uni-dentate carbonate species with IR bands at 1390 and 1520 cm⁻¹ [28–30]. For the 15CoMg catalyst, strong IR bands of the bi- and uni-dentate carbonate species on the MgO support dominate the spectrum and additional IR bands are not evident. Furthermore, the IR bands of the carbonate species on the MgO support appear to be of reduced intensity. Thus, the reduction temperature, loading and support affect the adsorption of CO₂ to form carbonate species on the supported cobalt catalysts considered in the present study.

3.4.2. Carbon dioxide hydrogenation reaction by *in situ* DRIFT and simultaneous reactivity measurement

3.4.2.1. Effect of reduction temperature. The effect of catalyst reduction temperature on the CO₂ hydrogenation reaction was studied over the 15CoAl catalysts and the spectra are shown in Fig. 9A. The

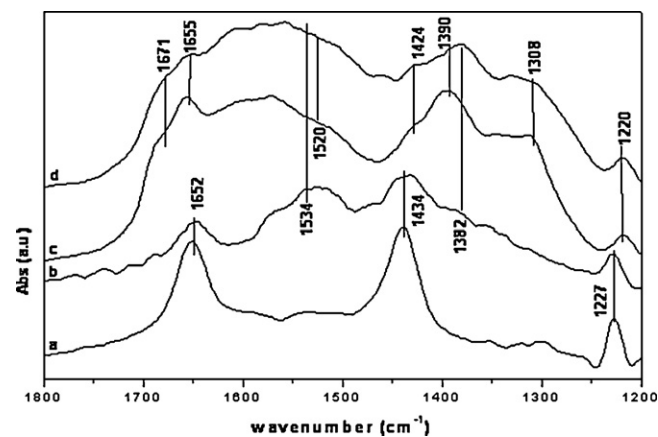


Fig. 8. *In situ* DRIFT spectra of CO₂ adsorption at 533 K over the supports and 15 wt% supported catalysts reduced in hydrogen at 823 K; (a) Al₂O₃, (b) 15CoAl, (c) MgO, and (d) 15CoMg.

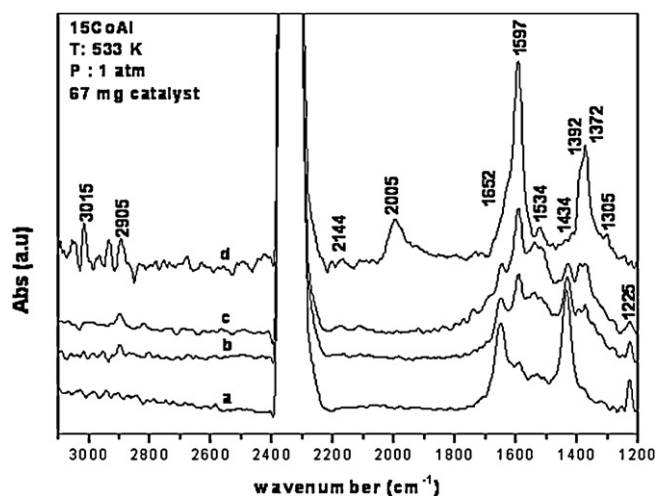


Fig. 9A. *In situ* DRIFT spectra of the CO₂ hydrogenation reaction at 533 K and 1 atm. pressure over 15CoAl catalysts calcined at (a) 773 K and reduced in hydrogen at (b) 623 K, (c) 723 K, and (d) 823 K.

CO₂ hydrogenation reaction over the freshly calcined 15CoAl sample is included as a reference. The corresponding CO₂ conversions and methane yields were measured from the outlet of the reaction cell and the results are shown in Fig. 9B. Fig. 9A reveals that for the freshly calcined 15CoAl catalyst, bicarbonate bands arising from the alumina support was observed. With an increase in reduction temperature the bicarbonate and carbonate bands intensity gradually decreases and new IR bands at 1305, 1372, 1392, 1534, 1597, 2005, 2144, 2905, and 3015 cm⁻¹ were observed. The bands at 2005 and 2144 cm⁻¹ correspond to linearly adsorbed and gas phase CO, respectively [21]. The IR bands at 1305 and 3015 cm⁻¹, clearly observed in the catalyst reduced at 823 K correspond to the gas phase methane [21]. The remaining IR bands at 1372, 1392, 1597, and 2905 cm⁻¹ are to the adsorbed formate species [21,29]. With an increase in reduction temperature, the IR bands associated with the formate species increase. With an increase in reduction temperature, Fig. 10B reveals that the CO₂ conversions and methane yield also gradually increases.

The XRD patterns discussed above reveal that with an increase in reduction temperature the available metal sites gradually increase. These metal sites appear to be responsible for the increase in CO₂ adsorption with increase in reduction temperature. Furthermore,

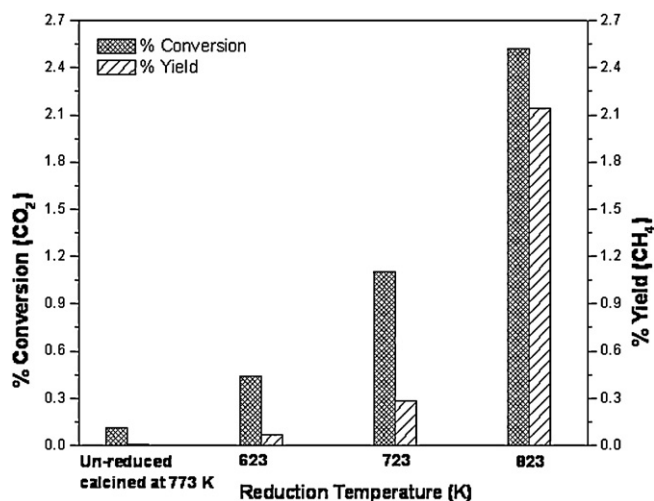


Fig. 9B. Corresponding reactivity data of the CO₂ hydrogenation reaction carried out over the catalysts given in Fig. 9A.

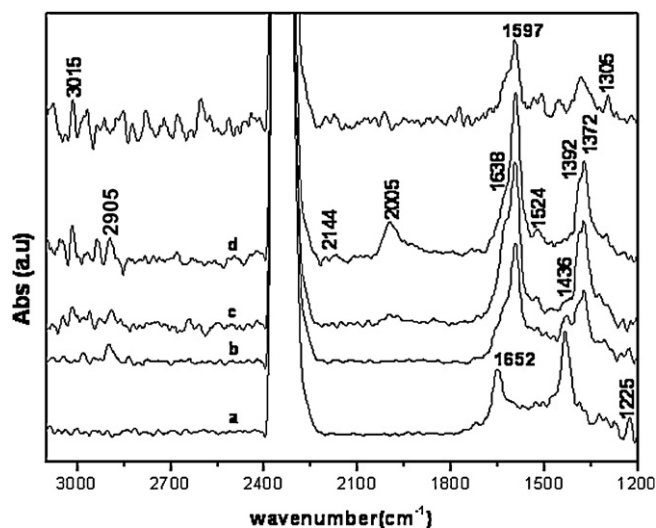


Fig. 10A. *In situ* DRIFT spectra of the CO₂ hydrogenation reaction at 533 K and 1 atm. pressure over xCoAl ($x = 5\text{--}20$ wt%) catalysts and Al₂O₃; (a) Al₂O₃, (b) 5CoAl, (c) 10CoAl, (d) 15CoAl, and (e) 20CoAl.

the corresponding reactivity measurement reveals that with an increase in the catalyst reduction temperature, the CO₂ conversion and methane yield also increases. Thus, the reduction temperature is a critical parameter for obtaining an active catalyst since the amount of metal sites available is directly linked with the reduction temperature. Considering the combined results from XRD, UV–vis–NIR, DRIFT and simultaneous reactivity studies it appears that 823 K is the most appropriate reduction temperature for synthesizing an active alumina supported cobalt catalyst. Furthermore, the linear adsorbed CO and adsorbed formate are the only stable species observed on the catalyst during the reaction. This does not discount the presence of additional transient species that may be formed during the reaction.

3.4.2.2. Effect of cobalt loading. The effect of cobalt loading on the CO₂ hydrogenation reaction was studied over the series of xCoAl catalysts and the results are shown in Figs. 10A and 10B. In Fig. 10A, the *in situ* DRIFT spectra and in Fig. 10B the corresponding reactivity data are shown. The spectrum of the CO₂ hydrogenation reaction over the alumina support is included as a reference in Fig. 10A. With increasing cobalt loading the formate band intensity

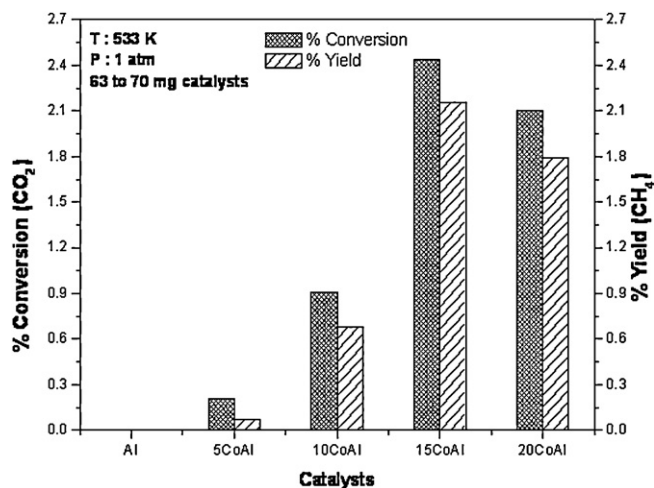


Fig. 10B. Corresponding reactivity data of the CO₂ hydrogenation reaction carried out over the catalysts given in Fig. 10A.

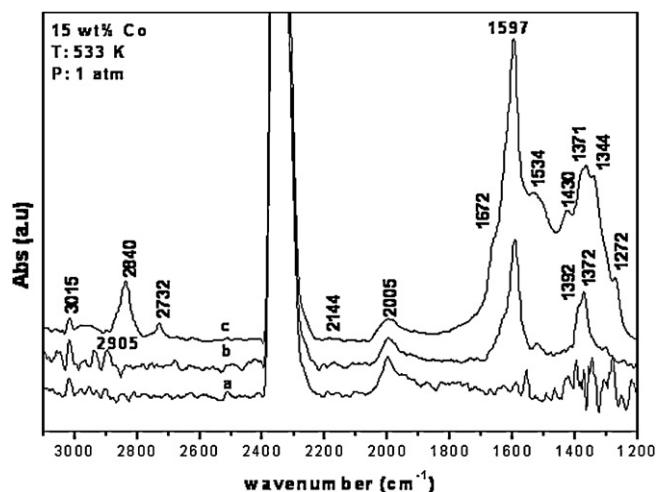


Fig. 11A. *In situ* DRIFT spectra of the CO₂ hydrogenation reaction at 533 K and 1 atm. pressure over 15 wt% Co catalysts on various supports reduced in hydrogen at 823 K: (a) 15CoSi, (b) 15CoAl, and (c) 15CoMg.

gradually increases till the 15CoAl catalyst and then decreases for the 20CoAl catalyst. The adsorbed CO band appears for the 10CoAl catalyst, and is distinct for the 15CoAl catalyst. For the 20CoAl catalyst the adsorbed CO band is not evident. Gas phase methane bands are also evident for the 15CoAl and 20CoAl catalysts. The reactivity data reveals that as a function of cobalt loading the CO₂ conversion and methane yield increases till the 15CoAl catalyst, where it is maximum, and then is about constant for the 20CoAl catalyst.

3.4.2.3. Effect of supports. The effect of support on the CO₂ hydrogenation reaction was also studied over 15 wt% supported cobalt catalysts and the results are shown in Figs. 11A and 11B. Linearly adsorbed CO was observed in all the spectra of supported catalysts containing 15 wt% of cobalt. For 15CoSi, no other band was evident. For 15CoAl and 15CoMg, however, additional IR bands were observed. For 15CoAl catalyst, and as discussed above, the additional IR bands corresponding to adsorbed formate and gas phase methane. For the 15CoMg catalyst, adsorbed carbonate, bicarbonate and formate species were observed; with the formate bands shifted to lower frequencies [31]. In addition to these species, bands at 1272 and 1672 cm⁻¹ were also observed. The bands at 1272 and

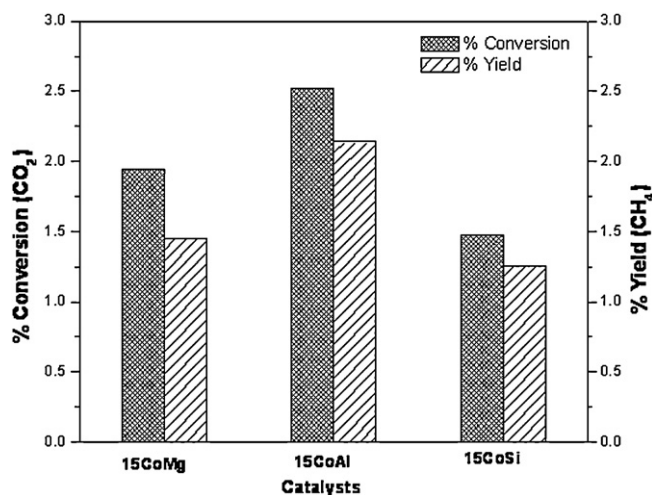


Fig. 11B. Corresponding reactivity data of the CO₂ hydrogenation reaction carried out over the catalysts given in Fig. 11A. Catalysts possess equal volume, however, the mass is different.

1672 cm⁻¹ appear to be due to the formation of strongly-bound chemisorbed formic acid [26,27] or bi-dentate carbonate of CO₂ on the basic support [30].

Fig. 11B reveals that CO₂ conversion and methane yield are the highest for 15CoAl, followed by 15CoMg and is the lowest for 15CoSi. However, it was noted that the amount of catalyst was different. The 15CoSi catalyst had the least density and completely filled the sample cup. The same amount, 30 mg, of 15CoAl and 15CoMg was loaded in the sample cup and the reactivity data was also collected. Using equal amounts of catalyst it was observed that the CO₂ conversion and methane yield was the highest for 15CoAl followed by 15CoSi and the 15CoMg catalyst possessed the lowest activity and yield. Correlating the reaction data with the corresponding species in Fig. 11A suggests that the presence of surface formate species is not necessary for CO₂ conversion or methane formation. Furthermore, IR bands of the formate species are shifted for the 15CoAl and 15CoMg catalysts. The shift in the formate bands for the different cobalt supported catalysts suggests that the formate species is formed on the metal–support interface. Furthermore, there appears to be a relationship between the intensities of the formate and carbonate species for the series of CoAl catalysts and the 15CoSi catalyst. It appears that the formate and carbonate species require the presence of an exposed support surface that assists in their formation. Though the cobalt metal and carbonate species are not clearly evident in the XRD and DRIFT studies, the formation of the formate species for the 15CoMg sample suggests the presence of cobalt metal in this catalyst. Thus, the role of the support is crucial for the formation and stabilization of the formate species, though the presence of a stable formate species is not a requirement for a supported cobalt catalyst to be active during the CO₂ hydrogenation reaction. The metal associated carbonate species appears to be the precursor for the formate species observed over the alumina supported cobalt catalyst.

4. Conclusion

Several alumina, silica, and magnesia supported cobalt catalysts were synthesized by the incipient wetness impregnation method and calcined at 773 K. The synthesized catalysts and supports were characterized and studied for the CO₂ hydrogenation reaction to understand the effect of the reduction temperature, cobalt loading and oxide support. It is observed that the surface area decreases with the addition of cobalt to the alumina and silica supports; however, for the magnesia supported catalysts the surface area increases. The ambient UV–vis–NIR spectra reveal the presence of CoAl₂O₄ at a calcination temperature of 973 K and cobalt–magnesia solid solution at 1173 K. Below 973 K the presence of CoAl₂O₄ is not evident. Furthermore, the XRD patterns and UV–vis–NIR spectra obtain under ambient conditions reveal that the reduction of the supported Co₃O₄ phase present in the different freshly calcined alumina supported cobalt catalysts appears to be complete at 823 K. At intermediate reduction temperatures the Co₃O₄ phase is converted to Co/CoOOH and then to cobalt metal. For the silica supported cobalt catalyst the reduction of the supported Co₃O₄ phase is incomplete at 823 K.

DRIFT studies suggest that CO₂ adsorption occurs as bicarbonate species on the alumina and magnesia support, and as carbonate species on the cobalt sites supported on alumina. The carbonate species increases with cobalt loading on this alumina support up to a cobalt loading of 15 wt%. No carbonate species was observed over the silica supported cobalt catalyst and for the magnesia supported cobalt catalyst the carbonate species on the support dominate. The three supported cobalt systems are active for the CO₂ hydrogenation reaction. The DRIFT spectra of the CoSi catalysts during the CO₂ hydrogenation reaction revealed the presence of only chemisorbed

CO. The CoAl and CoMg catalysts, however, revealed the presence of adsorbed formate and chemisorbed CO species during the CO₂ hydrogenation reaction. The adsorbed formate species increases with cobalt loading, up to 15 wt% cobalt, for the series of CoAl catalysts. The support appears to be responsible for the formation of the carbonate and formate species over the supported cobalt catalysts; however, formate formation is independent of the CO₂ conversion and methane yield. The formate species appears to be formed over the metal–support interface and the support plays a role in stabilizing it. It also appears that the conversion of CO₂ and methane yield increases with the reduction temperature up to 823 K and increasing cobalt loading up to 15 wt% for the alumina supported cobalt catalyst. The alumina supported catalysts possessed the highest methane yield compared to the silica and magnesia supported catalyst for the 15 wt% loading of cobalt under the present operating conditions.

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