

## Surface characterization of silica supported ceria catalysts

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**Abstract:** A characteristic feature of fluorite structured ceria, CeO<sub>2</sub>, is ability to undergo oxidation-reduction cycles in a perfectly reversible fashion. Silica supported ceria catalysts was prepared by impregnating of silica support with an aqueous solution of diammonium hexanitrocerrate [(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>] to yield final material containing 3 and 10 wt % CeO<sub>2</sub> catalysts. The samples thus obtained was calcined at 500 °C for 3 h. The materials were characterized by X-ray diffractometry (XRD), UV-Vis diffuse reflectance (DRS), N<sub>2</sub> – adsorption at 77 K, and infrared spectroscopy (IR). XRD showed the formation of nanocrystallites of ceria on silica surface (8.1-11.2 nm) when the amount is higher than 3 wt %; at lower loading ceria was found to be dispersed on the surface of silica. The surface area of the support was decreased by increasing the ceria loading level.

**Keywords:** Ceria/silica, XRD, N<sub>2</sub>-sorption, DRS and IR spectroscopy.

## Introduction

Metal oxides are widely used in the field of heterogeneous catalysis, both as catalysts and as supports for the so-called monolayer-type catalysts. In such applications the performance is determined by parameters like bulk metal oxide, surface area, the surface oxide structure and surface acidity [1–6]. Accordingly metal oxides must have high stabilities as well as high surface areas under conditions of their use both as catalysts and as support materials [7–9]. Silica is well known and commonly used support material due to its high surface area, also it is mostly inert carrier; furthermore the active supported phases can be obtained in well dispersed forms [10,11]. Thus, it is the most widely used as a support in several chemical industries [5,12].

A characteristic feature of fluorite-structured ceria, CeO<sub>2</sub> is its ability to undergo oxidation-reduction cycles in a perfectly reversible fashion [13]. Non stoichiometric ceria (CeO<sub>2-x</sub>) may be obtained with high departure from perfect stoichiometry when heated at ≥ 770 K in air, in vacuo or hydrogen atmosphere, without detectable departure from original structure [14-16]. Therefore, it has been utilized as a solid electrolyte for fuel cells [17] a reduction for the release of H<sub>2</sub> gas from water [13], and an important component in commercially available automobile exhaust-gas catalytic converters [18].

The wide application of ceria is due to its unique acid-base and redox properties. It is well known that ceria can affect; (i) the thermal and structure stability of the catalyst carriers [19]; (ii) the dispersion of supported metal [20,21]; (iii) the oxidation and reduction of noble metals [22]; (iv) the store and release oxygen in ceria containing catalysts [23] and (v) the decrease of carbon formation on the catalyst surface [24] etc. The high oxygen storage capacity (OSC) is a result of the high reducibility of Ce<sup>4+</sup>, which is a consequence of the O<sup>2-</sup> high mobility inside the ceria fluorite type lattice [25,26].

Accordingly, the present studies were undertaken to prepare (under mild thermal conditions) and characterize ceria supported on alumina. The dispersion of ceria particles was followed by X-ray diffractometry and UV-Vis diffuse reflectance spectroscopy. In-situ IR spectroscopy of adsorbed pyridine was used to probe surface acid sites.

## Experimental Section

### Materials

Silica (200 m<sup>2</sup>/g), as a support material, was Degussa product. It is commercially known as Aerosil-200, and according to the manufacturer is void of particle porosity. It is amorphous to x-ray diffractometry. Highly pure diammonium hexanitrocerrate (DAHC) [(NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] 99.9 % product of Aldrich] were used for the preparation of unsupported cerium oxide as well as the make up of the impregnating solutions. Unsupported CeO<sub>2</sub> was obtained by calcination of diammonium hexanitrocerrate at 773 K for 3 h.

Supported ceria catalysts were prepared by the impregnation method. The impregnating solution was prepared by dissolving a calculated amount of the catalyst parent compound, DAHC, in a suitable volume of distilled water (25 cc/g support) to give the required load (3 and 10 wt%-CeO<sub>2</sub> on SiO<sub>2</sub>). 1-g portion of support material was added slowly into 25 ml of impregnating solution of the required concentration, while being continuously stirred for 1 h. Then, the resulting suspension was allowed to settling for 1 h. Excess water was evaporated at 370 K. Impregnated supports thus yielded were further dried at 380 K till constant weight. Supported ceria catalysts on silica (CeSi) were obtained by calcination at 770 K for 3 h of the corresponding impregnated supports

### X-ray powder diffractometry (XRD)

X-ray powder diffractograms were recorded using a JSX-60PA Jeol diffractometer (Japan), equipped with Ni-filtered CuK<sub>α</sub> radiation (λ = 1.54056 Å) and operated at 35 kV and 20 mA. The diffraction patterns, derived as relative intensity (I/I<sup>0</sup>) versus d-spacing were compared. For identification purposes, the observed diffraction patterns were matched with standard diffraction data (ASTM). The crystallite size was estimated using the line broadening technique [27] and Williamson-Hall method [28].

### UV-Vis diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectra (DRS) were recorded over a wavelength range from 900 to 200 nm on a double-beam Shimadzu spectrophotometer model UV-2100 equipped with a diffuse reflectance attachment. Specpure BaSO<sub>4</sub> (Shimadzu) was the reference material for the calcined catalysts and the silica support. The DR spectra were not used for quantitative

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measurements; therefore, they were not converted to the Kubelka-Munk function [29].

### Nitrogen Sorptometry

Nitrogen adsorption-desorption isotherms at 77 K were determined automatically, using a multi-station high-speed gas sorption analyzer, Nova 2200 (Quntachrome Corporation, USA) volumetric instrument. Adsorbents were pre-out gassed at 393 K and  $5 \times 10^{-5}$  Torr for 3 h, and the reproducibility of the isotherms were better than 99%. The surface area ( $S_{BET}$ ) was determined from the nitrogen adsorption isotherm.

### Infrared spectroscopy

Infrared (IR) transmission spectra were recorded with a Genesis II FT-IR spectrophotometer, Mathson (USA). A self-supporting wafer (20-30 mg/cm<sup>2</sup>) of test samples mounted inside a specially designed transmission cell [30], allowing in situ pretreatment at temperature up to 773 K in a static gas atmosphere, was employed. The pretreatment conditions were as follows: heating in a stream of O<sub>2</sub> atmosphere at 450 °C for 1 h, followed by evacuation at 723 K for 1 h. Subsequently, the wafer was cooled to room temperature under dynamic vacuum, and the cell and wafer background spectra were recorded over the frequency range 4000-1000 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup>. IR spectra of adsorbed pyridine (Py) on test samples were obtained following exposure of the wafer to 5 Torr of Py vapor at various temperatures (RT-570 K) for 5 min, pumping off the gas phase at the same temperature for 5 min, and cooling to room temperature. The spectra of irreversibly adsorbed Py species were then obtained by absorbance-subtraction of the test sample background spectrum.

## Results and Discussion

### Evaluation of surface area

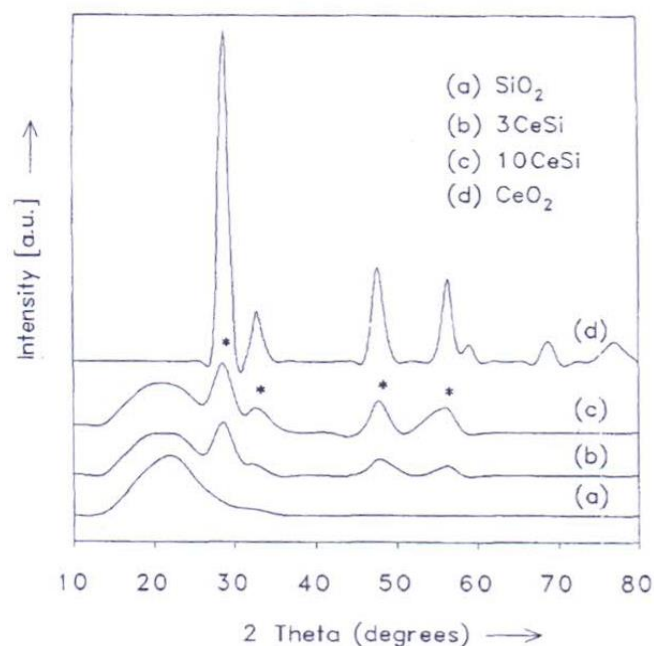
The BET surface area of supports and unsupports are given in Table. 1. The surface areas SiO<sub>2</sub> not changed after calcination at 770 K for 3 h, which are the similar with the reported data. Also, the surface area of CeO<sub>2</sub> is the similar with the results obtained by Zaki et al. [31]. Table. 1 show the BET surface areas of calcined supported catalysts at different loading levels. The surface areas of supported ceria catalysts show gradually decrease with increasing the amount of CeO<sub>2</sub> added to SiO<sub>2</sub>. With respect to the loading level of CeO<sub>2</sub>, one observes that the surface area decrease as the loading level increases. However, magnitude of the decrease is certainly related to unsupports and supports being used.

**Table 1.** Surface area of supports and supported catalysts after calcination at 770 K.

Catalyst	$S_{BET}$ m <sup>2</sup> /gm
SiO <sub>2</sub>	205
CeO <sub>2</sub>	21
3CeSi	185
10CeSi	165

### X-ray powder diffractograms

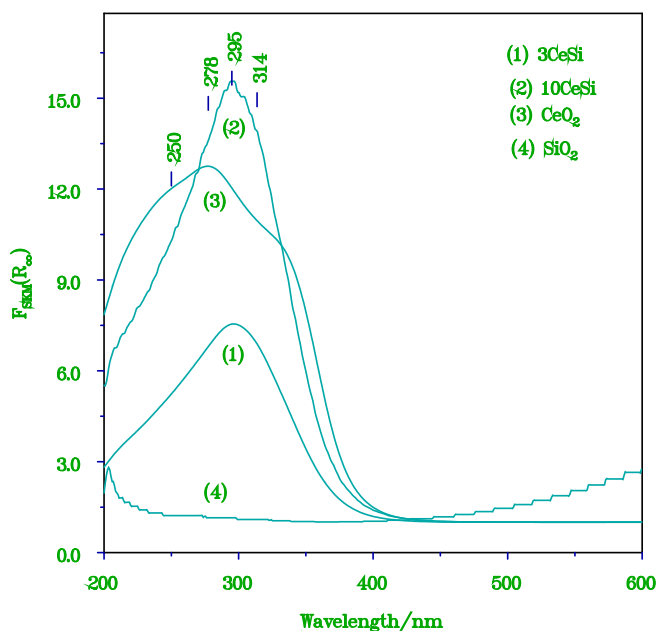
The XRD analyses of the calcined CeO<sub>2</sub>/SiO<sub>2</sub> at 770 K for 3 h catalysts at different loading levels samples are shown in Fig. 1. The XRD pattern of SiO<sub>2</sub> display only broad structure suggesting amorphous SiO<sub>2</sub>. The CeO<sub>2</sub>/SiO<sub>2</sub> at low loading level (3CeSi) display weak diffracted peaks for CeO<sub>2</sub> phase, but in case of high loading level the spectrum of 10CeSi display strong diffracted peaks for CeO<sub>2</sub> phase. It is clear that weak diffraction peaks corresponding to the four strongest peaks of fluorite structured CeO<sub>2</sub> are visible in the range 28-60° in the diffractograms of silica supported cerias. Also, the pattern of silica have been appeared. The lines of this pattern, when matched with the standerd data compiled in the ASTM Card No. 4-0593, disclose the formation of CeO<sub>2</sub> phases.



**Fig. 1.** X-ray powder diffractograms for silica supported cerias (CeSi), the silica support and unsupported ceria.

### UV-Vis diffuse reflectance spectroscopy (DRS)

The DR spectra given rise by the catalysts selected 3 and 10CeSi are given in Fig. 2. The DR spectra of CeO<sub>2</sub> and SiO<sub>2</sub> are inset for comparison. The DR spectra of CeO<sub>2</sub>/SiO<sub>2</sub>. Fig. 2 show three maxima at 250, 278 and 314 nm. The latter two maxima may be caused by Ce<sup>4+</sup> ← O<sup>2-</sup> chrg transfer (278 nm) and interband (314 nm) [32] is most likely due to Ce<sup>3+</sup> ← O<sup>2-</sup> chrg transfer [33,34]. When 3CeSi is examined, the absorption edge is blue-shifted from 400 nm to near 378 nm and the maximum at 250 nm is largely suppressed. These changes are slightly reversed upon examining the higher loaded 10CeSi. Such shifts are expected when a transition metal is diluted in a "hard" matrix, which causes the transition metal to be more ionic than when clustered with its own kind. The data obtained from DR spectra of CeO<sub>2</sub>/SiO<sub>2</sub> was in good agreement with the results obtained from XRD for the same samples for detecting the bulk phase of CeO<sub>2</sub>.

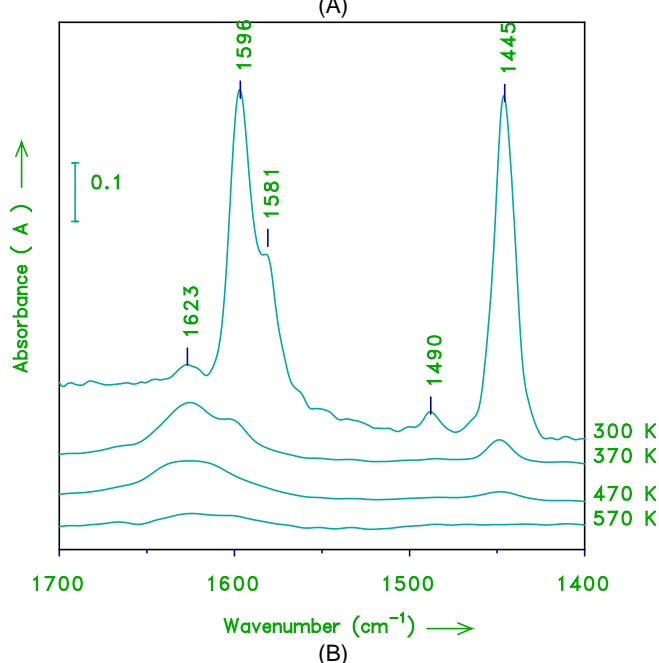
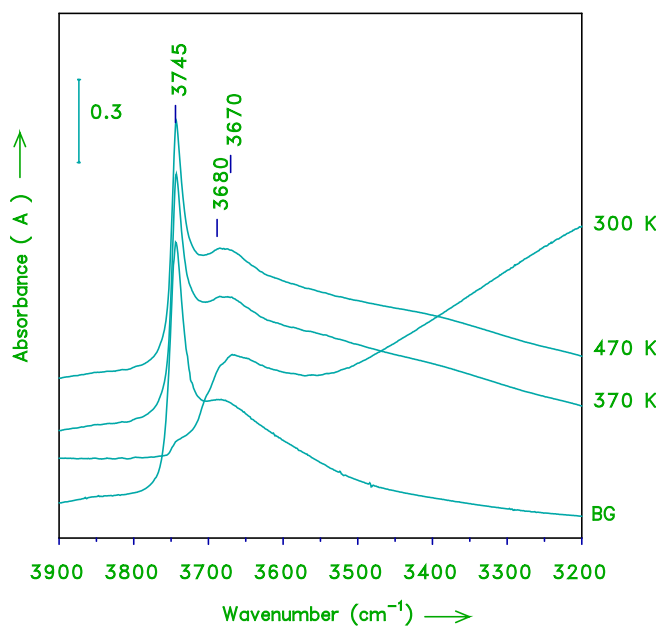


**Fig. 2.** UV-Vis diffuse reflectance spectra for silica supported cerias (CeSi), the silica support and unsupported ceria.

### Surface acidity of silica supported ceria catalysts

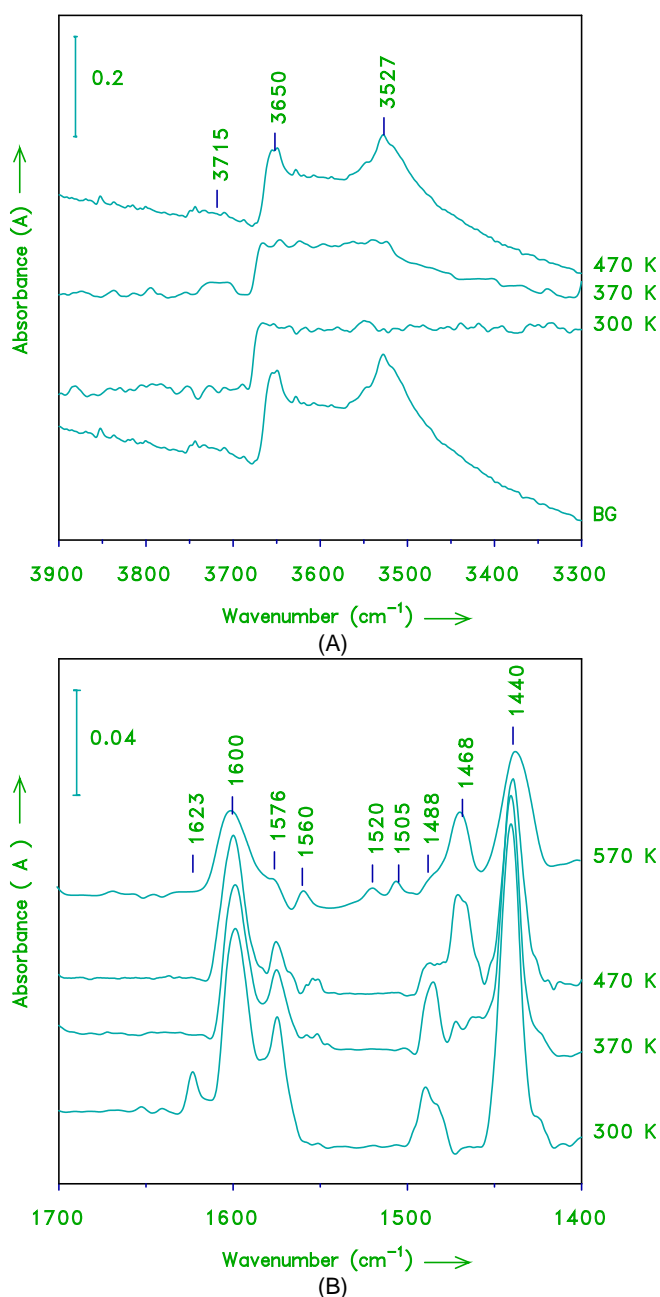
After recording the  $\text{SiO}_2$  background spectrum, Py vapour was introduced at 300 K and maintained in contact with the  $\text{SiO}_2$  catalyst for 10 min. The cell was then evacuated for 10 min, and spectra recorded over two ranges the first range at  $3900\text{--}3200\text{ cm}^{-1}$  and the second range at  $1700\text{--}1400\text{ cm}^{-1}$ . Figs. 3 A and B show the spectra of adsorbed Py on  $\text{SiO}_2$  at different ranges see above. Fig. 3 A shows the spectra of adsorbed Py on  $\text{SiO}_2$  over range of hydroxyl groups at 300, 370, and 470 K. The spectrum of adsorbed Py at 300 K on  $\text{SiO}_2$  show decreases in intensity of silanol band at  $3745\text{ cm}^{-1}$  and band at  $3673\text{ cm}^{-1}$ , while an intense and broad band develops at  $3015\text{ cm}^{-1}$  on adsorption of Py, the reduction of intensity of silanol group and appeared new band at  $3015\text{ cm}^{-1}$  indicate that the Py is physisorbed and formed hydrogen bond with the surface of hydroxyl groups of  $\text{SiO}_2$ . IR spectra of adsorbed Py at different thermoevacuation temperatures are shown in Fig. 3 A, we observed from the Fig. 3A that the intensity of silanol group increases in intensity by increasing the thermoevacuation temperatures and the band at  $3015\text{ cm}^{-1}$  disappeared again.

Fig. 3B exhibits the spectra taken from Py adsorbed on  $\text{SiO}_2$  ( $1700\text{--}1400\text{ cm}^{-1}$ ) following adsorption at 300 K and thermal desorption at 370, 470 and 570 K. The 300 K spectrum Fig. 3B exhibits five bands at  $1623$ ,  $1596$ ,  $1581$ ,  $1445\text{ cm}^{-1}$ , and weak band at  $1490\text{ cm}^{-1}$ . According to the analytical bands characterization of adsorbed Py these bands assigned to hydrogen bonded and physisorbed pyridine on the surface hydroxyl groups of  $\text{SiO}_2$ , which in agreement with the shifts in hydroxyl group at 300 K. Upon thermoevacuation, and as the temperature applied was increased from 370 to 570 K, the absorption intensities of these bands decreased continuously to the extent of complete elimination at 570 K. In the mean time, no other features are to be observed at 570 K. There is no evidence for a band at  $1540\text{ cm}^{-1}$ , indicates proton acidity and this in agreement with Roev [35], which he reported that no proton acidity on  $\text{SiO}_2$  by IR spectra of adsorbed  $\text{NH}_3$ ; and the shift of the band at  $1445\text{ cm}^{-1}$  is not large enough to indicate the Lewis acidity.



**Fig. 3.** IR spectra taken following Py adsorption on  $\text{SiO}_2$  at different temperature in: (A) vOH region ( $3900\text{--}3200\text{ cm}^{-1}$ ) of  $\text{SiO}_2$  and (B) vCCN region ( $1700\text{--}1400\text{ cm}^{-1}$ ).

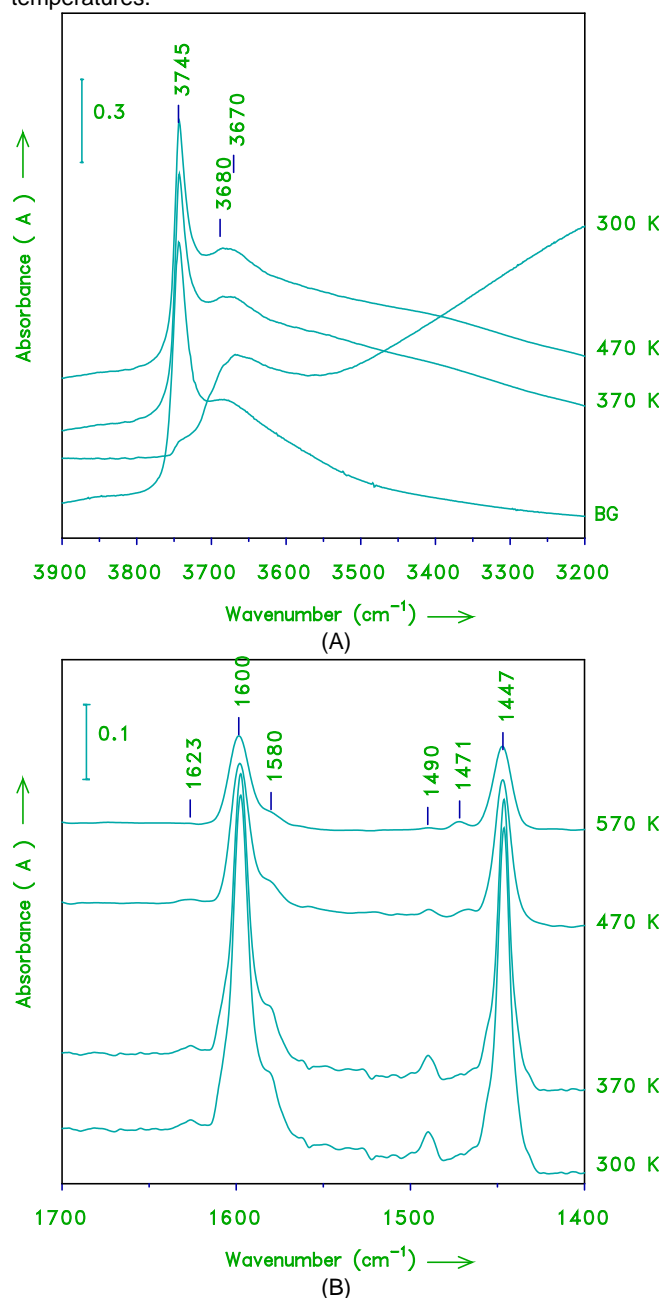
A spectra of adsorbed Py on  $\text{CeO}_2$  were recorded over two ranges similar to supports are shown in Figs. 4 A and B. The IR background spectrum of hydroxyl groups of ceria display three bands at  $3715$ ,  $3650$  and  $3527\text{ cm}^{-1}$ . Also, Fig. 4A show the spectra of Py adsorbed at different temperatures. After adsorption of Py at 300 K (Fig. 4A) the vOH groups were shifted to lower frequencies. The shifts in hydroxyl groups disappeared and the original background spectrum of  $\text{CeO}_2$  appeared again by increasing the thermoevacuation temperature to 370 K, are shown in Fig. 4 A.



**Fig. 4.** IR spectra taken following Py adsorption on CeO<sub>2</sub> at different temperature in: (A) vOH region (3900-3300 cm<sup>-1</sup>) of CeO<sub>2</sub> and (B) vCCN region (1700-1400 cm<sup>-1</sup>).

Spectra were taken of Py irreversible held at room and high temperatures on CeO<sub>2</sub> catalyst over range 1700-1400 cm<sup>-1</sup> are shown in Fig. 4B. The spectrum of adsorbed Py at 300 K display five bands (Fig. 4 B) at 1623 cm<sup>-1</sup> and 1489 cm<sup>-1</sup> (medium), 1600, 1576 cm<sup>-1</sup> (strong) and very strong band at 1440 cm<sup>-1</sup>. According to analytical assigned bands of adsorbed Py, these bands are due to coordinated Py with aprotic acid sites on the surface of CeO<sub>2</sub>. The occurrence of the 8a mode at two different frequency (1623 and 1595 cm<sup>-1</sup>) may indicate that an aprotic acid sites involved assume two different acidity strengths [31]. Fig 4B show the spectra at different thermoevacuation temperatures from 370 K to 570 K. These spectra in Fig. 4 B show common feature of gradual weakening in intensity of the bands characteristic of the 300 K adsorbed species of Py by increasing the thermoevacuation temperatures. At  $\geq 470$  K the band at 1580 cm<sup>-1</sup> shifted to 1600 cm<sup>-1</sup> and the band at 1489 cm<sup>-1</sup> reduced in intensity only small feature of this

band is still over the surface. Also, new bands were observed at high temperatures these bands are 1558, 1520, 1505 and 1468 cm<sup>-1</sup> are shown in Fig. 4 B. According to Zaki. et al. [31], these bands are due to cracking of Py on the surface of CeO<sub>2</sub> at high temperatures.



**Fig. 5.** IR spectra taken following Py adsorption on 3CeSi at different temperature in: (A) vOH region (3900-3300 cm<sup>-1</sup>) of 3CeSi and (B) vCCN region (1700-1400 cm<sup>-1</sup>).

The IR spectra of adsorbed Py on the surface of 3CeSi are shown in Figs. 5A and B. Hydroxyl IR spectra of adsorbed Py on the surface of 3CeSi are shown in Fig. 5A. The background spectrum of 3CeSi is inset for comparison and reveals two bands at 3745 and 3685 cm<sup>-1</sup>, these bands characteristic to the surface free and bridged hydroxyl groups of SiO<sub>2</sub> surfaces (see above in case of SiO<sub>2</sub>). The bands characteristic to hydroxyl groups of CeO<sub>2</sub> was not observed on the surface of 3CeSi. The adsorption of Py at 300 K was shown in Fig. 5A, display decreases in the intensity of unperturbed silanol group at 3745 cm<sup>-1</sup> and new band at 3660 cm<sup>-1</sup>, due to physisorbed [36] Py on the surface of

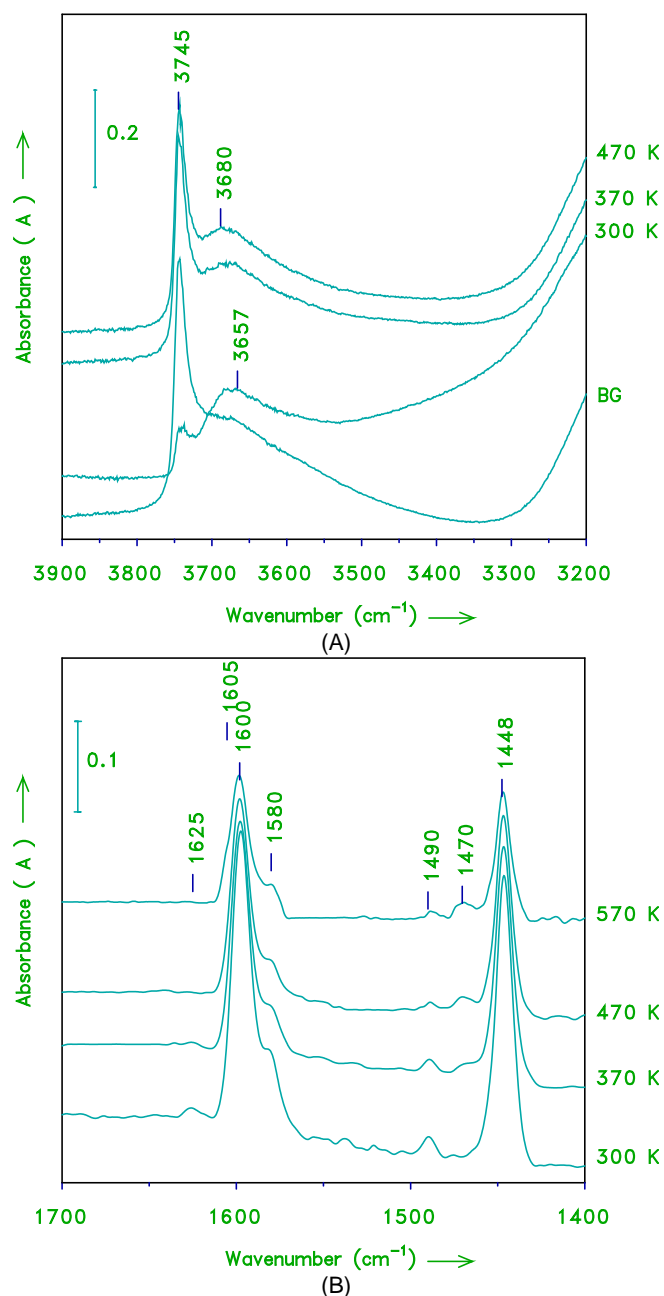
hydroxyl groups of 3CeSi. In addition to band at  $3000\text{ cm}^{-1}$  was observed on the surface of 3CeSi due to strong hydrogen bond formation with acidic hydroxyl groups on the surface. This band also was observed on  $\text{SiO}_2$  surface at 300 K. This means that the surface of  $\text{CeO}_2$  hydroxyl groups on 3CeSi has no effect on the acidic hydroxyl groups of pure  $\text{SiO}_2$ . The intensity of silanol group increased by increasing the thermoevacuation temperatures and the band at  $3000\text{ cm}^{-1}$  was disappeared.

The spectra of chemisorbed Py on the 3CeSi sample at different temperatures are shown in Fig. 5B. The spectrum of adsorbed Py at 300 K display five bands at 1598 and  $1445\text{ cm}^{-1}$  (very strong); and two weak bands at 1490 and  $1623\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ . These bands are characteristics to hydrogen bonding and coordinated Py with acidic site on the surface of 3CeSi. The presence of 8a mode by two different frequencies may be due to two different types of Lewis sites on the surface of 3CeSi. The spectrum of adsorbed Py at 370 K reflected the bands characteristics adsorbed Py on 3CeSi at 300 K by decreased in the intensity. At 470 K the spectrum of adsorbed Py reflected four bands at 1600, 1580, 1490 and  $1447\text{ cm}^{-1}$  these bands are due to coordinated Py with Lewis acid site on the surface of 3CeSi, with small feature at  $1473\text{ cm}^{-1}$ . The band at  $1623\text{ cm}^{-1}$  was removed at 470 K. The observation of Py species with 8a mode at  $1600\text{ cm}^{-1}$  which remained after evacuation at 470 K is sufficient for identification of a strongly chemisorbed species, coordinated at (strong) Lewis centers. The presence of aprotionic center on the surface of 3CeSi are due to presence of  $\text{Ce}^{4+}$  on the surface of 3CeSi. The spectrum at 570 K display three bands at 1600, 1580 and  $1447\text{ cm}^{-1}$  are due to coordinated Py with strong Lewis acid centers on the surface of 3CeSi. In addition to one band was observed at  $1471\text{ cm}^{-1}$  this band we have observed on pure  $\text{CeO}_2$  and may be is due to craking of Py on the surface of  $\text{CeO}_2$  in 3CeSi.

The spectra of adsorbed Py on 10CeSi at different temperatures are shown in Figs. 6 A and B. The hydroxyl IR spectra of adsorbed Py are shown in Fig. 6A. The spectrum of adsorbed Py at 300 K on 10CeSi are similar with the spectrum of adsorbed Py on 3CeSi at 300 K. The spectrum in Fig. 6A display decreased in the intensity of silanol group and new band appeared at  $3657\text{ cm}^{-1}$  is due to physisorbed Py [32]. The shifts in silanol group on 10CeSi similar with the shift OH's bands on 3CeSi and  $\text{SiO}_2$ . The intensity of silanol group increased with increasing the thermoevacuation temperatures to reached the original spectrum at 470 K. The band at  $3010\text{ cm}^{-1}$  is due to the formation hydrogen bonding with the silanol group was removed by increasing the temperature see above in the Fig. 6A.

The coordinated Py on the aprotionic sites on the surface of 10CeSi at different thermoevacuation temperatures are shown in Fig. 6B. Spectrum of adsorbed Py at 300 K in Fig. 6 B display five absorption bands at 1625 (weak), 1598 (strong), 1580 (medium), 1490 (weak) and very strong band at  $1445\text{ cm}^{-1}$ . These bands we were observed on 3CeSi at 300 K, and are due to the hydrogen bonded with acidic hydroxyl groups and coordinated Py with aprotionic acid sites on the surface. The presence of 8a mode at two different frequency values ( $1625$  and  $1598\text{ cm}^{-1}$ ) may indicated that the aprotionic acid sites involved assume two different acidity strengths [31]. The intensity of these bands are strong than the intensity of the bands were observed on 3CeSi and this means that the surface of 10CeSi is strong in acidity than 3CeSi. The spectrum of adsorbed Py at 370 K reflected the similar bands of adsorbed Py on 10CeSi at 300 k with decreased in the intensity of these bands. The spectrum of adsorbed Py at 470 K display strong

bands at 1600 and  $1448\text{ cm}^{-1}$  with weak band at  $1580\text{ cm}^{-1}$ , these bands are due to coordinated Py with strong aprotionic acid sites on the surface. In addition to one band at  $1470\text{ cm}^{-1}$  we have observed on 3CeSi. The spectrum of Py on 10CeSi at 570 K display the similar spectrum at 470 K, in addition to one band at  $1605\text{ cm}^{-1}$  are due to strong aprotionic acid sites on the surface of 10CeSi. The occurrence of the aprotionic acid sites on the surface of 10CeSi are due to the presence of  $\text{Ce}^{4+}$  on the surface of 10CeSi and by increasing the amount of  $\text{CeO}_2$  on  $\text{SiO}_2$  surface increased the aprotionic acid sites on the surface of  $\text{SiO}_2$ .



**Fig. 6.** IR spectra taken following Py adsorption on 10CeSi at different temperature in: (A) vOH region ( $3900\text{--}3200\text{ cm}^{-1}$ ) of 10CeSi and (B) vCCN region ( $1700\text{--}1400\text{ cm}^{-1}$ ).

## Conclusions

Bulk characterization of supported CeO<sub>2</sub> catalysts and IR spectroscopy of adsorbed basic probes as Py leads to the following conclusions:

- 1) Unsupported ceria prepared by calcination of (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] at 770 K for 3 h consists of fluorite-structured crystallites.
- 2) The BET surface area of supported catalysts decreases with increasing the added amount of support.
- 3) The CeO<sub>2</sub> phase were detected by XRD and DRS on the calcined CeO<sub>2</sub>/SiO<sub>2</sub>.
- 4) UV-Vis diffuse reflectance spectroscopy show no peaks for Ce<sup>4+</sup>-Ce<sup>3+</sup> interaction on the surface of SiO<sub>2</sub>.
- 5) Ceria surfaces expose aprotic acid sites at least two different acidity strengths as well as two types of OH<sup>-</sup> groups
- 6) The adsorption of Py on the surface of CeO<sub>2</sub>/SiO<sub>2</sub> show that the aprotic acid sites increase by increasing the amount of CeO<sub>2</sub> on SiO<sub>2</sub>. No peridinium ion species was observed on the surface of CeO<sub>2</sub>/SiO<sub>2</sub>. The stability of Py at high temperatures decreased by decreasing the amount of CeO<sub>2</sub> on the surface.

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