

EFFECTS OF SODIUM HYDROXIDE TREATMENT ON COORDINATION CHANGES OF COBALT IONS IN CoNaY BY MEANS OF UV/VIS DIFFUSE REFLECTANCE SPECTROSCOPY

Jong-Dae Han and Seong-Ihl Woo*

Department of Chemical Technology, College of Engineering, Changwon National University,
9, Sarim-dong, Changwon, Kyungnam 641-773, Korea

*Department of Chemical Technology, Korea Advanced Institute of Science and Technology,
373-1, Kusong-dong, Yusong-gu, Taejon 305-701, Korea

(Received 9 March 1993 • accepted 22 July 1993)

Abstract—The coordination changes of Co^{2+} in CoNaY/NaOHs, prepared by cobalt ion-exchange and treatment with NaOH, during dehydration at various temperatures have been investigated by UV/VIS diffuse reflectance spectroscopy. After dehydration of CoNaY/NaOHs at 473 K, the DRS bands show the formation of mixed cobalt oxide species interacted with lattice oxygen. This mixed cobalt oxide species interacted with lattice oxygen decompose during further dehydration at 673 K. The strong intensities of the bands at 660, 575 and 530 nm after dehydration of CoNaY/NaOHs at 873 K indicate that a considerable amount of the cobalt ions remains in the sodalite cage with tetrahedral coordination even after dehydration at 873 K.

INTRODUCTION

Zeolites can play an important role in industrial catalysis, due to their shape-selective character, high surface area, acidic nature, and well-defined structure. The most common technique for introducing metals into zeolites is that of ion exchange and subsequent reduction with a suitable reducing agent [1,2]. The reducibilities of the transition metal ions in zeolites is related to the electrochemical potential of the metal ions [3], the location of ions in the structure [4,5-7] and the amount of OH groups in the zeolite [8]. Cobalt ions in CoNaY zeolite are more likely to stay in hexagonal prisms(site S_I) or sodalite windows(site S_{II}) after dehydration, where they can be stabilized by higher number of coordination to the zeolite lattice [9]. A high reduction temperature is, therefore, required to achieve a reasonable degree of reduction, causing the formation of large cobalt clusters on the exterior surface of zeolite and destruction of the zeolite crystal.

Ham and Woo reported [10] a new method of preparing Y-zeolite supported cobalt catalysts, which provides an enhancement in the reducibilities of cobalt ions by migrating cobalt ions in the sites S_I and S_{II}

to the sodalite cage and supercage. This method is based on the contacting cobalt exchanged zeolites with excess aqueous alkali metal hydroxide solution and washing with deionized water to remove any remaining alkali metal hydroxide from the zeolite pores. The reducibility of resulting product depends upon the concentration of sodium hydroxide and the cobalt-loading. Chung et al. [11,12] reported an enhancement of reduction by injecting of alkali solution into the pores of the zeolite after dehydration. They washed the catalysts with dilute alkali solution after injection of alkali solution. In those catalysts, excess alkali metals remain in the pores of zeolite and the alkali effects, such as, modification of electronic properties [13] and ensemble effect [14] may work. Han and Woo reported [15] the coordination changes of Co^{2+} in Y-zeolite prepared by ion-exchange and dehydration at various temperatures by means of UV/VIS diffuse reflectance spectroscopy.

In this work we investigated the effects of sodium hydroxide treatment on the coordination changes of Co^{2+} ions in Y-zeolite during dehydration at elevated temperatures.

EXPERIMENTAL

For preparation of catalysts, the sodium form of

*To whom all correspondences should be addressed.

zeolite Y of Strem Chemicals, Inc. (USA, lot No. 10779-s) was used. It was pretreated with 0.1 N sodium chloride aqueous solution to remove the sodium deficiency in NaY. The chloride was washed out from the zeolite structure with deionized water until no chloride was detected with silver nitrate in the filtrate. This pretreated NaY was ion-exchanged with aqueous 0.05 N $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (pH 5) at 363 K for 12 hr to prepare ion-exchanged catalyst CoNaY. After ion exchange, catalysts were filtered and washed with flowing deionized water until the unused ion was removed, then dried at 383 K in air. The amount of cobalt ions exchanged was measured by atomic absorption analysis. The loading of cobalt was indicated by the number in front of abbreviation, *i.e.* 5CoNaY (5 wt% cobalt loading at wet basis). CoNaY was treated with sodium hydroxide by contacting with various concentrations of sodium hydroxide solution at room temperature for 5 min (the weight ratio of hydroxide solution to CoNaY was 200). After treatment with sodium hydroxide, the catalysts were filtered and washed with deionized water to remove any remaining sodium hydroxide from the zeolite pores. Then the catalysts were dried at 383 K in air for 5 hr. The amount of alkali metal in the solution is shown as a suffix of the catalyst name (*i.e.* 5CoNaY/2NaOH, 2 is the ratio of the number of Na atoms to those of cobalt). For preparation of $\text{CoO}(\text{OH})$, the aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was mixed with sodium hydroxide solution at room temperature and the precipitate was filtered and washed with deionized water. Then the precipitate was dried at 383 K in air for 5 hr. This precipitate was used for $\text{CoO}(\text{OH})$. These samples were stored in a desiccator saturated with ammonium chloride solution. The details of the experimental procedures for diffuse reflectance spectroscopy (DRS) spectra have been described elsewhere [15].

RESULTS AND DISCUSSION

The spectra of the fully hydrated samples of 5CoNaY, 5CoNaY/NaOH's (NaOH-treated 5CoNaY's), $\text{CoO}(\text{OH})$ and Co_3O_4 are shown in Fig. 1. The spectra of 5CoNaY has an absorption band at about 520 nm, which is typical of the hexa-aquo-cobalt ion complex arising from the ligand-field transition rhombohedrally distorted octahedral cobalt ion complex [16]. The intensities of absorption bands at 390 nm and 750 nm increase with increasing NaOH concentration. This absorption bands can be ascribed to cobaltic hydroxide. The $\text{CoO}(\text{OH})$ shows bands at 390 and 750 nm in Fig. 1 (f). The spectrum of 5CoNaY/30NaOH after calcination

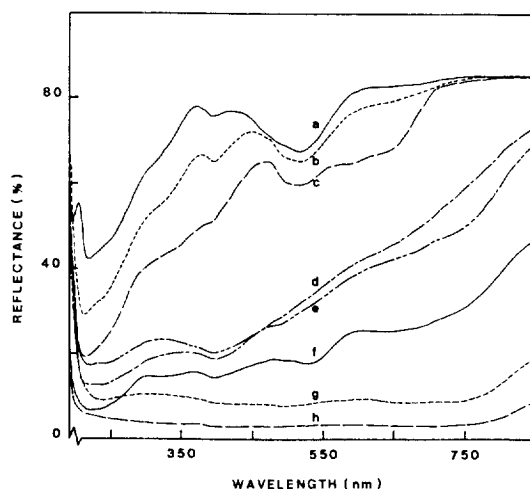


Fig. 1. DRS spectra of fully hydrated samples.

(a) 5CoNaY, (b) 5CoNaY/0.7NaOH, (c) 5CoNaY(cal)/30NaOH, (d) 5CoNaY/2NaOH, (e) 5CoNaY/30NaOH, (f) $\text{CoO}(\text{OH})$, (g) 5CoNaY/30NaOH calcined at 623 K for 1 hr, (h) Co_3O_4 .

at 623 K for 1 hr in air [Fig. 1(g)] is similar to that of Co_3O_4 [Fig. 1(h)], suggesting that the hydroxylated cobalt was converted to Co_3O_4 during calcination. Ashley and Mitchell [17] reported that the electronic transitions of CoO and Co_3O_4 supported on alumina are represented by the bands at 227, 285 and 381 nm, and at 220, 270 and 370 nm respectively. The absorption band around 300 nm observed in the DRS spectra might be ascribed to the charge-transfer transition of cobalt oxides.

The spectra of 5CoNaY/0.7 NaOH dehydrated at various temperatures are shown in Fig. 2. After dehydration at 383 K, the spectra [Fig. 2(b)] shows the presence of tetrahedral Co^{2+} indicated by absorption bands at 630, 575 and 530 nm [9]. After dehydration at 473 K, the absorption band at 630 nm is shifted to 660 nm indicating the change of the ligand in Co^{2+} ions as reported elsewhere [9, 15]. During dehydration at 673 K, the intensities of the bands at 660, 575, and 530 nm [Fig. 2(d)] decrease slightly and a shoulder peak at 720 nm appears. After dehydration at 873 K, the absorption intensity of band at 720 nm increases and the intensities of the bands at 660, 575 and 530 nm decrease a little more. However, the intensities of bands at 660, 575 and 530 nm are still strong after dehydration at 873 K indicating that a considerable amount of the cobalt ions remains in the sodalite cage with tetrahedral coordination. For the tetrahedral complexes, the visible spectrum corresponding

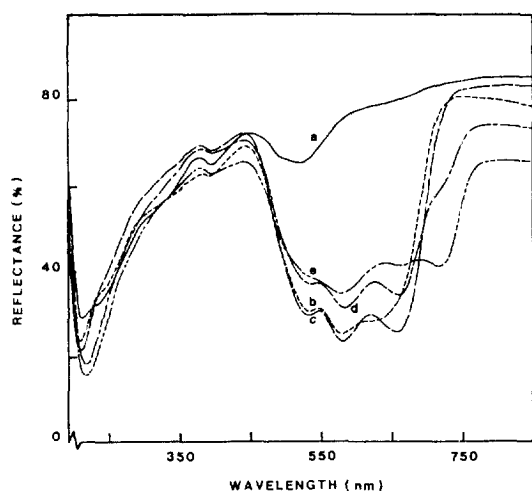


Fig. 2. DRS spectra of 5CoNaY/0.7NaOH.

(a) fully hydrated sample (—), (b) dehydrated for 1 hr at 10^{-6} torr and at 383 K (---), (c) at 473 K (···), (d) at 673 K (- · -), (e) at 873 K (- - -).

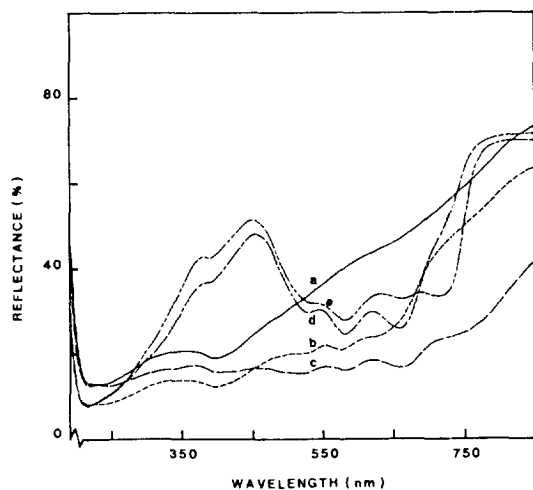


Fig. 3. DRS spectra of 5CoNaY/2NaOH.

(a) fully hydrated sample (—), (b) dehydrated for 1 hr at 10^{-6} torr and at 383 K (---), (c) at 473 K (···), (d) at 673 K (- · -), (e) at 873 K (- - -).

to the highest energy transition between the nondegenerate ground state $^1A_1(F)$ and the triply degenerated excited state $^1T_1(P)$ is split into three symmetrically spaced peaks by the Jahn-Teller effect [18]. In the CoNaYs, not treated with sodium hydroxide, the bands at 720 nm has been assigned Co^{2+} ions migrated into the hexagonal prism where they experience a distorted octahedral environment [19]. The intensity at

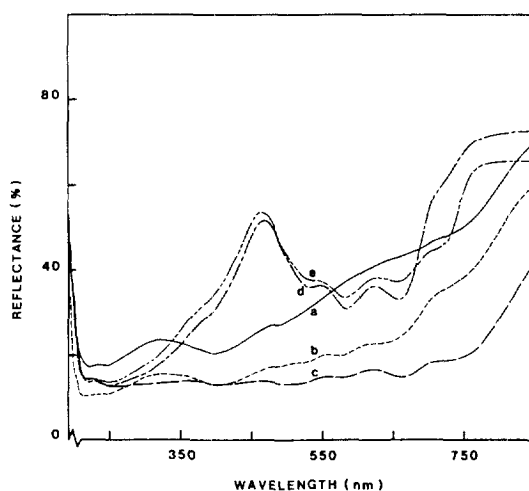


Fig. 4. DRS spectra of 5CoNaY/30NaOH.

(a) fully hydrated sample (—), (b) dehydrated for 1 hr at 10^{-6} torr and at 383 K (---), (c) at 473 K (···), (d) at 673 K (- · -), (e) at 873 K (- - -).

720 nm in Fig. 2 is too strong to consider that the band at 720 nm is due to the Co^{2+} ions migrated into the hexagonal prism because the intensity of crystal field transition absorptions for octahedral cobalt is 100 times lower than that of tetrahedral cobalt [15, 20]. The band at 720 nm might be due to the tetrahedral cobalt ions in oxide environments, which may be bridged Co-O-Co in the sodalite cage formed by dehydration of the $(CoOH)^+$ that was proposed by IR data elsewhere [10]. The intensity of the band at 720 nm is partially due to the octahedral Co^{2+} in hexagonal prism. The portion of Co^{2+} in hexagonal prism was estimated by TPR method described elsewhere [10].

The spectra of 5CoNaY/2NaOH and 5CoNaY/30NaOH dehydrated at various temperatures are shown in Fig. 3 and Fig. 4, respectively. After dehydration at 383 K, the spectra [Fig. 3(b) and Fig. 4(b)] show weak absorption bands at 630, 575 and 530 nm. After dehydration at 473 K, the absorption band at 630 nm is shifted to 660 nm indicating the change of the ligand in Co^{2+} ions as in the case of 5CoNaY/0.7NaOH. During dehydration at 383 K, the increase of band intensity at 390 and 750 nm can be attributed to the conversion of unoxidized $Co(OH)_2$ to $CoO(OH)$ because $CoO(OH)$ has bands around 390 and 750 nm. After dehydration at 473 K, the absorption bands at 390 and 750 nm may be attributed to the formation of mixed cobalt oxide species interacted with lattice oxygen. After further dehydration at 673 K, the intensities of the bands at 390 and 750 nm considerable decrease. The bands

at 660, 575 and 530 nm are resolved more clearly and a shoulder peak at 720 nm appears. The decrease in intensities of the bands at 390 and 750 nm may be attributed to the decomposition of cobalt oxide species interacted with lattice oxygen because Co_3O_4 does not decompose by dehydration. The more clearly resolved bands at 660, 575 and 530 nm show tetrahedral cobalt ion form. After dehydration at 873 K, the intensities of the bands at 660, 575, 530 and 390 nm decrease slightly and show strong band intensity at 720 nm. The bands at 660, 575, and 530 nm indicate the presence of tetrahedral cobalt ions located in the sodalite cage [9]. The intensities of the band at 720 nm after dehydration at 873 K of 5CoNaY/NaOH's [Fig. 1(e), Fig. 2 (e) and Fig. 3(e)] are very strong in comparison with those of CoNaY's not treated with NaOH [15]. The intensity of the band at 720 nm after dehydration at 873 K decreases with increase in the NaOH concentration. During dehydration at 873 K the cation(CoOH)⁺, observed in the IR spectrum of NaOH-treated catalysts [10], might produce a bridged cation system(Co-O-Co) as reported by Uytterhoeven and Schoonheydt [21]. The intensity of crystal field transition absorption for octahedral cobalt is 100 times lower than that of tetrahedral cobalt [15, 20]. Han and Woo reported [10] from TPR data that the 5CoNaY/NaOH's show the portion of Co^{2+} in sodalite cage(site S_T and S_T') is larger than that in hexagonal prism. From these reasons, the band at 720 nm after dehydration at 873 K may be assigned tentatively to a bridged Co-O-Co in the sodalite cage with tetrahedral coordination and partially to octahedral Co^{2+} in the hexagonal prisms. The strong bands arising from tetrahedral cobalt ion will mask the weaker bands of octahedral cobalt ions. However, this explanation requires further evidence.

During dehydration at 673 and 873 K after calcination of 5CoNaY/30NaOH at 623 K for 1 hr no change is shown [this spectra is same as the Fig. 1(g)]. This suggests that the cobaltic hydroxide is converted to Co_3O_4 during calcination and the colour of the sample is too dark to observe absorption bands. Pure oxide (CoO) and many oxides of Co^{2+} exhibit absorption at 400-370 nm [17]. The intensity of the band at 390 nm after dehydration at 673 and 873 K increases with increasing the NaOH concentration. The band at 390 nm may be attributed to cobalt oxide species [17]. The CoO(OH) is converted to Co_3O_4 at 421-423 K in vacuo [22]. This suggests that low concentration of NaOH is not enough to exchange cobalt ions completely. Hence, the formation of CoO(OH) was suppressed, which agrees with the previous results of TPR and IR investigations [10].

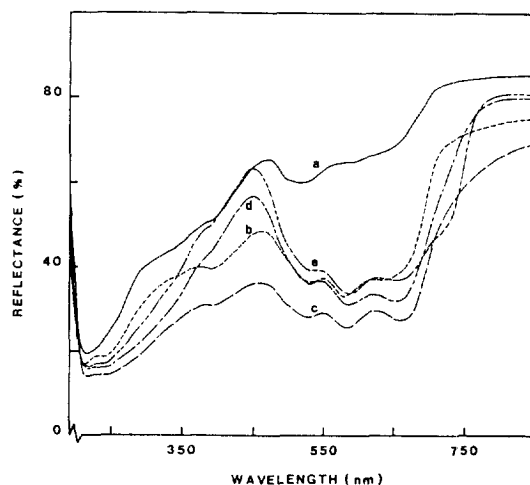


Fig. 5. DRS spectra of 5CoNaY(cal)/30NaOH.

(a) fully hydrated sample (—), (b) dehydrated for 1 hr at 10^{-6} torr and at 383 K (---), (c) at 473 K (···), (d) at 673 K (- · -), (e) at 873 K (- - -).

The spectra of 5CoNaY(cal)/30NaOH, treated with NaOH aqueous solution after calcination at 623 K for 3 hr, after dehydration at various temperatures are shown in Fig. 5. The spectra of the fully hydrated 5CoNaY(cal)/30NaOH shows Fig. 5(a)] absorption band at 520 nm and weak bands at 630, 575, 530 nm. The band at 520 nm indicates the presence of hexa-aquo-cobalt ion complex as shown in Fig. 1(a). The bands at 630, 575 and 530 nm indicate the presence of tetrahedral cobalt ions formed by migration of the cobalt ions inside supercage into the sodalite cage during calcination. After dehydration at 383 K, the spectrum [Fig. 5(b)] shows absorption bands at 630, 575 and 530 nm. After dehydration at 473 K, the absorption band at 630 nm is shifted to 660 nm indicating the change of the ligand in Co^{2+} ions similar to the case of non-calcined samples. During dehydration at higher temperature the spectra of 5CoNaY(cal)/30NaOH are similar to that of 5CoNaY/30NaOH [Fig. 4]. However, the absorption intensities at 390 and 750 nm of 5CoNaY(cal)/30NaOH after dehydration at 383 and 473 K are weaker than those of 5CoNaY/30NaOH. This indicates that the amount of CoO(OH) formed during the NaOH treatment of 5CoNaY precalcined at 623 K for 3 hr is less than that of CoO(OH) formed during the NaOH treatment of non-calcined 5CoNaY. The majority of the cobalt ions are located in sodalite cage and hexagonal prism after calcination, because the $\text{Co(H}_2\text{O)}_6^{2+}$ is dehydrated and migrated to the sodalite cage and the hexagonal prism during calcination. During

treatment with NaOH solution, only few of cobalt ions in the sodalite cage and hexagonal prism are substituted by Na^+ to form $\text{Co}(\text{OH})_2$. So, the amount of $\text{CoO}(\text{OH})$, resulted from oxidation of $\text{Co}(\text{OH})_2$, in $5\text{CoNaY}(\text{cal})/30\text{NaOH}$ is less than that of $5\text{CoNaY}/30\text{NaOH}$. These results agree with the TPR and IR results [10].

In a previous study, the amount of cobalt ions located at various sites were estimated from the area of each TPR peak [10]. Sodium hydroxide treatment of CoNaY provides an enhancement in the reducibilities of cobalt ions by migrating cobalt ions in the sites S_1 and S_7 to the sodalite cage and supercage. These DRS results of CoNaY/NaOH's consist with the TPR results and support that the enhancement in the reducibilities of cobalt ions resulted from migrating of cobalt ions in the pores of the zeolite.

CONCLUSIONS

The treatment of CoNaY's with aqueous sodium hydroxide solution induces the formation of cobaltic hydroxide. The formation of cobaltic hydroxide increases with increasing NaOH concentration of aqueous sodium hydroxide solution. This cobaltic hydroxide is converted to Co_3O_4 during calcination. During dehydration at 383 and 473 K of NaOH-treated CoNaY's a species of cobalt oxide interacted with lattice oxygen different from Co_3O_4 is formed. This cobalt oxide interacted with lattice oxygen decomposes to form tetrahedral cobalt ions during further dehydration at 673 K. DRS spectra of the NaOH-treated CoNaY's dehydrated at 873 K show that a considerable amount of the cobalt ions remains in the sodalite cage with tetrahedral coordination. The formation of cobaltic hydroxide is suppressed by calcining CoNaY at 623 K before NaOH treatment.

ACKNOWLEDGEMENT

This research was funded by KOSEF Puspose Oriented Fundamental Research (1990-1993).

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