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Reduction behavior and catalytic properties of cobalt containing ZSM-5 zeolites

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Abstract

The reduction behaviors and catalytic properties of cobalt containing ZSM-5 zeolites prepared by various methods were compared. Temperature-programmed reduction (TPR), X-ray diffraction and IR spectroscopy were the main techniques used for the study of reduction behavior. The existence of framework cobalt and small amounts of cobalt oxide in Co-ZSM-5 samples, which were prepared by incorporation of different amounts of cobalt into the zeolite synthesis gels, and cobalt silicate-like species in the Co/ZSM-5 sample, which was prepared by precipitating impregnation of cobalt oxide on ZSM-5, were therefore established. TPR studies indicated that both framework cobalt and cobalt silicate-like species required temperatures higher than 973 K to be reduced. The structure of Co-ZSM-5 was partially destroyed after reduction at temperatures higher than 1023 K, due to the removal of framework cobalt from the ZSM-5 structure. On the other hand, the reduction of cobalt silicate-like species in Co/ZSM-5 at 1023 K did not affect the zeolitic structure. As the cobalt loading in Co-ZSM-5 was increased, increasing amounts of extra-framework cobalt oxide were formed and well dispersed in the porous structure of zeolite. The catalytic activities of these cobalt-containing zeolites in carbon monoxide hydrogenation were found to be directly proportional to the amount of cobalt metal present. The latter was obtained from the reduction of cobalt oxide under pretreatment conditions. The acidity and shape selectivity of ZSM-5 accounted for the product selectivity.

Keywords: Carbon monoxide hydrogenation; Cobalt–ZSM-5; Reduction; Temperature-programmed reduction; X-ray diffraction; Zeolites

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1. Introduction

Metal containing zeolites have been used as catalysts for a wide range of chemical reactions, such as hydrogenation, oxidation, isomerization, and cracking of various organic feedstocks [1,2]. Possible applications of these materials in various chem-

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ical industrial processes have attracted considerable interest to investigate these systems. Furthermore, a combination of a Fischer–Tropsch metal, such as iron or cobalt, with ZSM-5 zeolite has resulted in bifunctional catalysts. These catalysts were found to exhibit improved selectivity for gasoline-range products, and therefore synthesis gas can be converted to gasoline-range hydrocarbons in one step [3–5].

The catalytic activity and selectivity of bifunctional catalysts were reported to be affected by the preparation methods. Rao and Gromley [5] compared the activities of cobalt–ZSM-5 catalysts prepared by two different methods and found that the selectivity to aromatics was higher with the catalyst prepared by methods of physically admixing. The lower selectivity to aromatics with the catalysts prepared by impregnation was attributed to the decrease in the number of Brønsted acid sites in the zeolites and a result of some cobalt in an ion-exchanged form.

By dispersing transition metals within the zeolite pore structures, a well dispersed metal phase is usually expected because the particle size of the metal will be limited to the pore dimensions. As a result, the catalytic behavior of the supported catalyst is expected to be different from those with chunks of metals [2,6]. In the literature, several methods have been investigated to prepare cobalt containing zeolites [7–9]: (1) decomposition of organometallic compounds on zeolites, (2) impregnation of zeolite with cobalt nitrate solution, (3) ion-exchange, and (4) incorporation of cobalt ions within zeolites during crystal growth. Rossin et al. [9] have reported different ways to incorporate cobalt into the ZSM-5 structure during the crystal growth procedure. By adding a cobalt containing amorphous aluminosilicate into the ZSM-5 synthesis gel, they obtained cobalt isomorphously substituted zeolites of high crystallinity. However, it was also found that these cobalt–ZSM-5 crystals had low activity in carbon monoxide hydrogenation.

The aim of this study is to identify the location and chemical nature of the cobalt species in cobalt containing ZSM-5 zeolites prepared by two different methods: (1) incorporation of cobalt in the zeolite synthesis gel, and (2) precipitating impregnation of a cobalt salt on zeolite crystals, and to elucidate their catalytic behaviors in carbon monoxide hydrogenation based on the characterization results.

2. Experimental

2.1. Synthesis

ZSM-5 zeolite with a Si/Al mole ratio of 140 was prepared according to the procedures described in the literature [10]. The molar composition of the gel was 10 Na_2O–20 TPABr–Al_2O_3–950 SiO_2–5300 H_2O, where TPABr is tetrapropylammonium bromide. The as-synthesized zeolite was calcined at 823 K in air for 12–16 h to decompose the TPA^+ ions, followed by NH_4^+-exchange with a 1 M NH_4Cl

solution four times. The proton form of ZSM-5 (H-ZSM-5) was obtained by calcining the ammonium form of ZSM-5 at 823 K for 12–16 h.

Co-ZSM-5 catalysts were prepared by adding a solution of cobalt sulfate into the aqueous mixture of water glass (Si source), TPABr and NaOH, followed by adjusting the pH value of the solution to 11 with sulfuric acid, and autoclaving at 453 K for two days. The samples in acid form were obtained through treatment similar to that mentioned for the preparation of H-ZSM-5. The Si/Co mole ratio was varied from 10, 40, to 80 based on the starting components.

A sample (termed Co/ZSM-5), with cobalt oxide impregnating precipitation on zeolite in a 1:10 weight ratio, was prepared by adding a 1 M Na_2CO_3 solution into a H-ZSM-5 zeolite suspension in hot (358–363 K) cobalt nitrate solution until a pH of 9.5 was reached. The solid was filtered, washed and calcined at 823 K, followed by ammonium ion-exchange again with NH_4Cl solution and calcination to ensure that the zeolite was in the proton form.

2.2. *Characterization*

X-ray powder diffraction patterns were obtained using a Philips 1840 X-ray diffractometer with Cu Kα radiation. The lattice parameters were determined with a Mac Science MXP3T X-ray diffractometer. The transmission IR spectra were obtained using KBr mixed pellets with a Perkin-Elmer 983 spectrometer. The diffuse reflectance spectra were taken with self-sustained wafers after heating at 673 K for 2 h to examine the OH stretching vibration using a Bomem MB155 FTIR spectrometer. Surface area measurement was based on the physical adsorption of nitrogen at 77 K using a volumetric system. Silicon and cobalt contents were determined by ICP-AES (Allied analytical systems, Model ICAP 9000) analysis on the dissolved samples.

Temperature-programmed reduction experiments were carried out in a home-built device. The reactor, consisting of a 1/4 in. O.D. quartz tube, was surrounded by a programmable furnace. A thermocouple placed directly in the sample bed was used to monitor continuously sample temperature. A sample of 100 mg was dried and degassed under dry nitrogen at 473 K, cooled to ambient temperature, followed by heating at a programmed rate of 10 K/min to 1113–1173 K in a 10% H_2/N_2 gas flow. The H_2/N_2 mixture gas was purified by passing through a copper based oxygen removal catalyst (BASF R3-11), followed by a molecular sieve trap. The flow-rates of the gases were monitored by mass flow controllers and meters. The flux of H_2/N_2 gas was maintained at a flow-rate of 25 cm^3/min. Hydrogen consumption was detected with a thermal conductivity detector (TCD), where the H_2/N_2 gas passed through the reference cell, forward to reactor and trap, then back to the sample cell of the TCD. A liquid-N_2–acetone trap, which was kept at a temperature of ca. 193 K, was placed at the out-stream of the reactor and was used for the removal of water formed during the temperature-programmed reduction (TPR) experiment.

Table 1
Elemental analysis data and BET surface areas of cobalt containing ZSM-5 zeolites

Samples	Si/Co (mol ratio)		Si/Al (mol ratio) solid	BET S.A. (m^2/g)
	Gel	Solid		
Co-ZSM-5/CP(10)	10	5.4	117	374
Co-ZSM-5/CP(40)	40	27	150	385
Co-ZSM-5/CP(80)	80	57	126	386
H-ZSM-5			140	366
Co/H-ZSM-5/IP			140	301

Temperature-programmed desorption (TPD) of ammonia was carried out with a DuPont 9900 thermogravimetric system. The catalyst was preheated at 823 K under dried nitrogen gas for 30 min, then cooled to ambient temperature for ammonia adsorption. After purging the physically adsorbed ammonia at 473 K, the TPD profile was obtained by heating the catalyst bed to 873 K at a heating rate of 10 K/min.

2.3. Reaction

The catalyst was reduced with a 10% H_2/N_2 gas flow (25 ml/min) at 673 K for 16–20 h. Then, the temperature of the catalyst was lowered to reaction temperature (573 K) under the H_2/N_2 atmosphere. The reactant gas ($H_2/CO=1$) was introduced and the pressure was slowly raised to 50 atm. A flow of 20 ml/min (under 1 atm) was maintained.

The products of the reaction were hydrocarbons, carbon dioxide and water. The liquid products were collected in a stainless steel tubular trap at room temperature under 50 atm, while the gaseous products and the unconverted feed gases were analyzed periodically using an on-line gas chromatograph. The liquid products collected in the first 8 h were abandoned since the Fischer–Tropsch reaction had a long induction period.

3. Results and discussion

Table 1 shows the BET surface areas and the elemental analysis results of Co-ZSM-5 samples with various cobalt loadings. The cobalt content in the solid is less than, but directly proportional to, that in the preparation gel, while the Al contents are in the range close to that of plain ZSM-5. They all have comparably high surface areas as that of H-ZSM-5. The color of the as-synthesized samples was pink to pale purple, but that turned to dark yellow after calcination at 823 K for 16–20 h. Because bulk cobalt oxide (Co_3O_4) is black, the dark yellow color suggests that the samples might contain some extra-framework cobalt oxide. Table 2 lists the lattice para-

Table 2
Lattice parameters of cobalt containing ZSM-5 zeolites prepared by co-precipitation

Samples	*a*	*b*	*c*	*β*	Volume
Co-ZSM-5/CP(10)	19.874	20.108	13.371	90.65	5342.9
Co-ZSM-5/CP(40)	19.874	20.105	13.370	90.66	5342.0
Co-ZSM-5/CP(80)	19.894	20.103	13.366	90.72	5345.0
H-ZSM-5	19.880	20.107	13.369	90.65	5343.6

monoclinic structure, length unit in ångstrom.

meters obtained from the powder X-ray diffraction patterns of Co-ZSM-5 samples, in comparison to those of H-ZSM-5. The data show that the lattice parameters as well as the unit cell volumes do not vary in a consistent pattern with the cobalt loading. These results are attributed to the disorder of lattice structures and decrease in crystallinity of these co-precipitated samples as the cobalt loading increases. However, the presence of cobalt ions in the framework was confirmed by the appearance of an extra absorption peak in the O–H stretching vibration region. Fig. 1 shows that H-ZSM-5 gives two peaks at 3598 and 3728 cm^{-1}, corresponding to

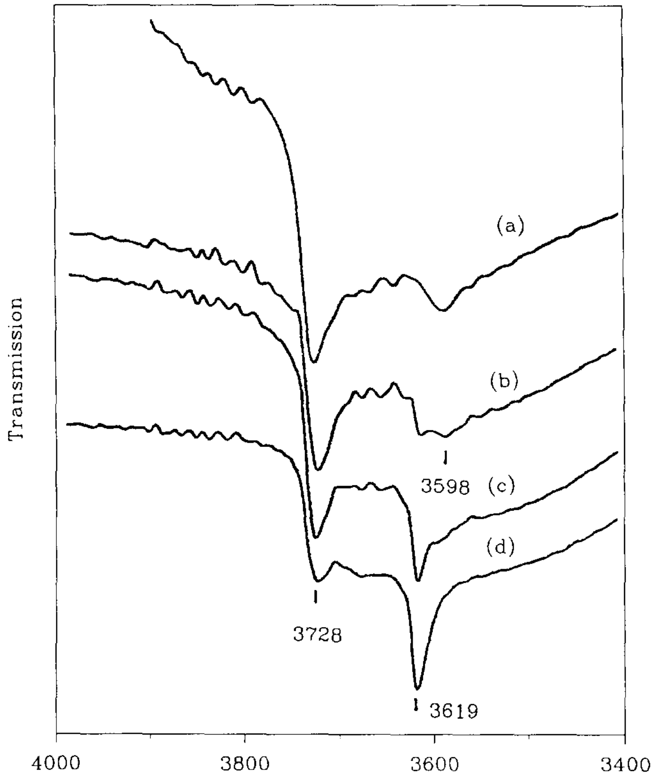


Fig. 1. Diffuse reflectance IR spectra of the OH stretching vibration region of H-ZSM-5 (a), and Co-ZSM-5 catalysts of Si/Co = 57 (b), Si/Co = 27 (c), and Si/Co = 5.4 (d).

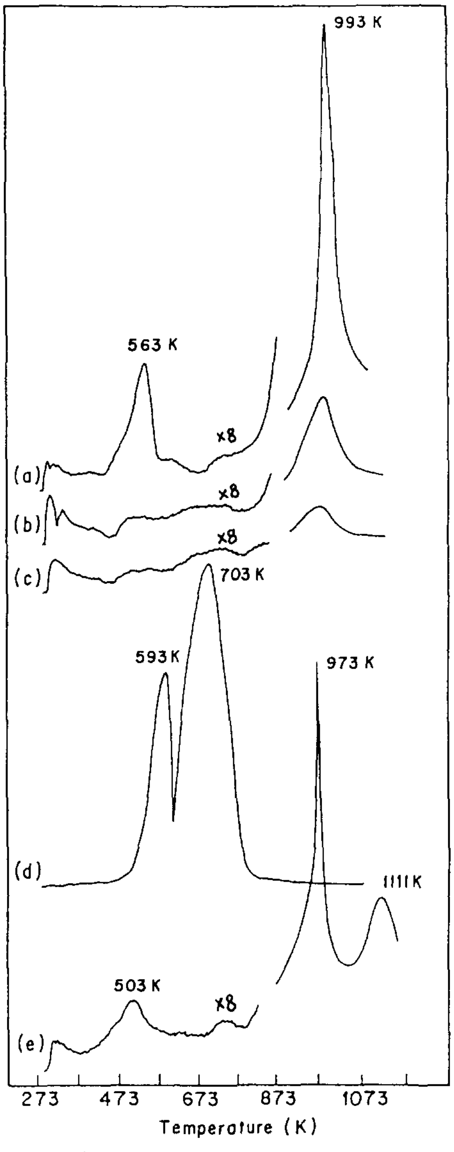


Fig. 2. TPR profiles of Co-ZSM-5 (Si/Co = 5.4) (a), Co-ZSM-5 (Si/Co = 27) (b), Co-ZSM-5 (Si/Co = 56) (c), Co_3O_4 (d), and Co/ZSM-5 (e).

the O–H groups adjacent to framework with Al^{III} substitution and the silanol groups, respectively. As Co^{II} ions were added to the synthesis gels, the resultant zeolite powders give an additional peak at 3619 cm^{-1}, and its intensity is directly proportional to the cobalt loading. For the Co/ZSM-5 sample which was prepared by precipitating impregnation, Table 1 shows that its BET surface area was obviously lower than that of the pristine zeolite. This fact is attributed to either portions of the zeolitic structure were destructed or the pores were blocked.

The TPR profiles of Co-ZSM-5 samples with various cobalt loadings are shown in Fig. 2a–c. For Co-ZSM-5 of highest cobalt content (Fig. 2a), the TPR profile contains a small peak at 563 K, and a strong peak with the maximum at 993 K. The latter actually extends to temperatures higher than 1113 K; in other words, the reduction was not complete even at 1113 K. The integrated areas of both TPR peaks decrease as the cobalt content is lowered. The integrator sensitivity for the low-temperature peak is eight times that of the high-temperature peak, and the area of the low-temperature peak is below 5% of the total area. Therefore, the species corresponding to low-temperature reduction are only a small portion of the Co-ZSM-5 samples. Moreover, these low-temperature peaks become very weak and nearly disappear for the samples with low cobalt content. Figs. 2b and 2c show that only two weak broad peaks appear at ca. 523 and 693 K, respectively.

The reduction behavior of Co-ZSM-5 was compared with that of the sample prepared by physically mixing Co_3O_4 and H-ZSM-5. Fig. 2d shows that the TPR profile of the latter sample gives two peaks at around 593 and 703 K. They are ascribed to the reduction of Co_3O_4 to CoO and that of CoO to Co metal, respectively. This result is consistent with the reduction behavior of bulk Co_3O_4 [11]. Accordingly, the small peak that appeared at 563 K in Co-ZSM-5 is likely due to the reduction of extra-framework cobalt oxide. Moreover, because this peak shifts to a lower temperature in comparison with that of the bulk Co_3O_4, the extra-framework cobalt oxide is probably in the form of very fine particles. On the other hand, the species reduced at ca. 993 K is attributed to framework cobalt or some other types of cobalt silicate since Roe et al. [12] reported that cobalt silicate required a temperature above 973 K to be reduced.

Fig. 2e shows the TPR profile of Co/ZSM-5 prepared by precipitating cobalt oxide onto ZSM-5 in alkaline solution. Surprisingly, the profile is very similar to that of Co-ZSM-5: a sharp peak at 973 K and a weak peak at 503 K. However, an additional peak raises around 1043 K with a maximum at ca. 1111 K. Puskas et al. [13] studied the system where cobalt oxide was precipitated on high surface area silica by neutralization of a nitrate solution. They found that cobalt silicates were formed and their reduction required temperatures higher than 973 K. Therefore, the species which were reduced at 973 K and 1111 K probably correspond to two kinds of cobalt silicates, which were formed by cobalt ions reacting with ZSM-5 framework in the precipitation impregnation process. On the other hand, the amount of cobalt oxide which should be reduced at low temperature (ca. 503 K) is only negligible.

In order to identify further the cobalt species in these samples, the X-ray diffraction (XRD) patterns and IR spectra of the samples reduced at various temperatures were examined. Fig. 3 shows the XRD patterns of Co-ZSM-5 (Si/Co mol ratio = 5.4) before and after reduction. The pattern before reduction is consistent with that of plain ZSM-5 with the intensity of the diffraction peaks being slightly weaker (Fig. 3a). In other words, the crystallinity of Co-ZSM-5 is somewhat lower than that of plain ZSM-5. Nevertheless, cobalt oxide was not detected in the pattern. The XRD pattern was hardly changed after Co-ZSM-5 was reduced at 793 K, but the intensity of the diffractogram decreased dramatically after 1023 K reduction

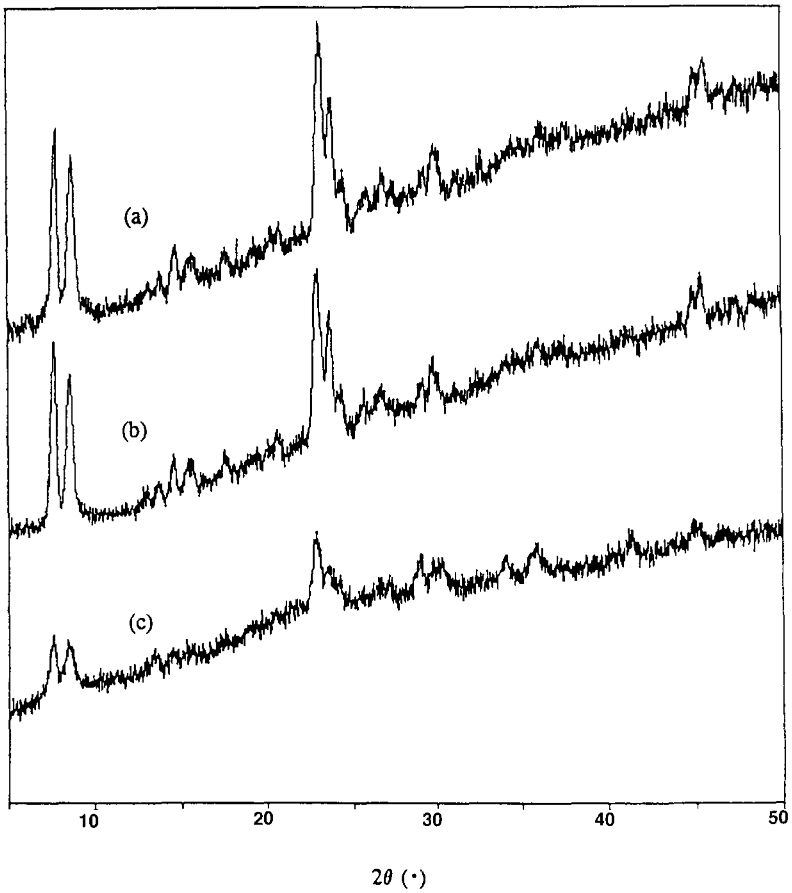


Fig. 3. XRD patterns of Co-ZSM-5 (Si/Co = 5.4) before (a), and after reduction at 793 K (b) and 1023 K (c).

(Fig. 3b and 3c, respectively). Therefore, the species which was reduced at 1023 K is likely to be cobalt incorporated in ZSM-5 framework. As cobalt was removed from the framework during the high-temperature reduction process, the zeolitic structure was largely broken down.

Fig. 4 shows the corresponding IR spectra of Co-ZSM-5 before and after reduction in comparison with those of Co_3O_4 and H-ZSM-5. The absorptions near 1100, 800, and 450 cm^{-1} are typical for high siliceous materials. According to the Flanigen–Khatami–Szymanski correlation [14,15], these peaks were assigned to internal vibration of Si, AlO_4 tetrahedra and were common to silica and quartz. The absorption at 650–550 cm^{-1}, on the other hand, was assigned to the presence of a double-ring of tetrahedra in the zeolitic framework [16]. For a ZSM-5 structure, the latter absorption appears near 550 cm^{-1}. The intensity ratio of the peaks at 550 cm^{-1} to 450 cm^{-1} is often used as a quantitative measurement of zeolite crystallinity [12]. For Co-ZSM-5 before reduction, a peak appeared at ca. 665 cm^{-1}, which is coincident with a strong absorption of Co_3O_4. This peak nearly disappeared after the sample was reduced at 793 K (Fig. 4c), and completely disappeared after

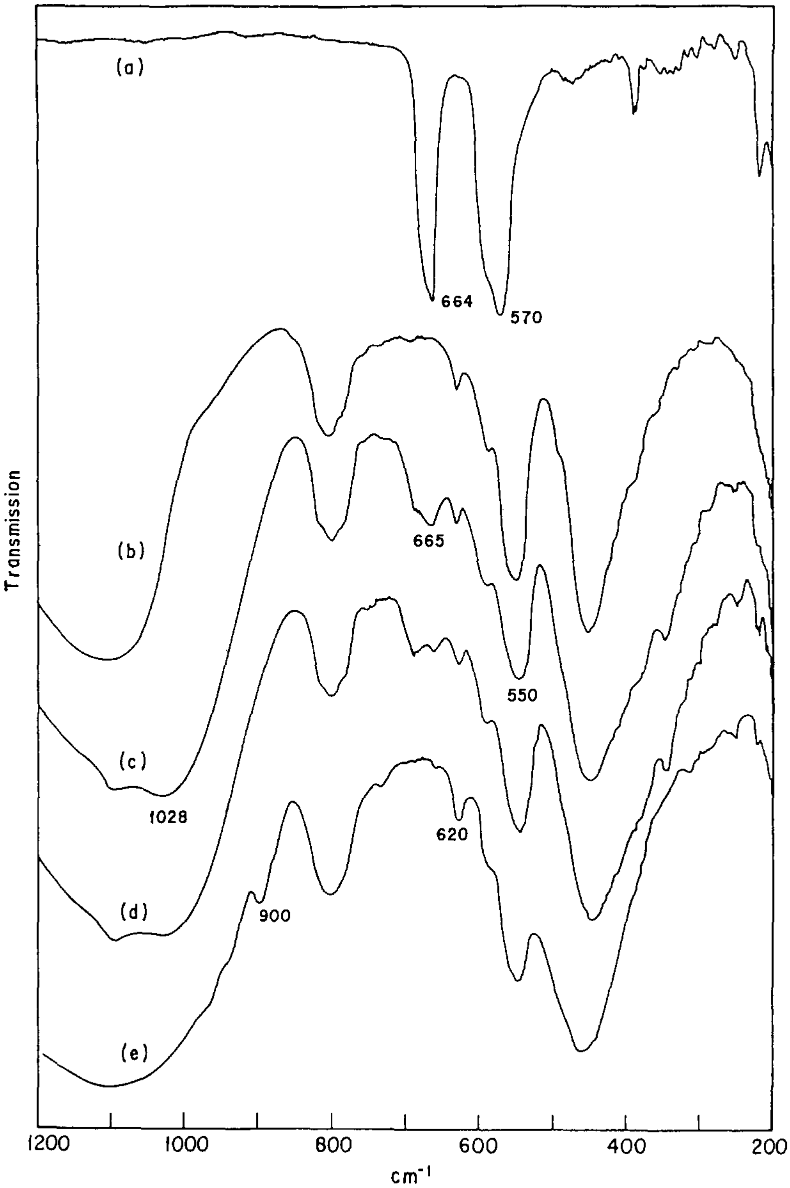


Fig. 4. IR spectra of Co_3O_4 (a); H-ZSM-5 (b); and Co-ZSM-5 (Si/Co = 5.4) before TPR (c), and after reduction at 793 K (d) and 1023 K (e).

reduction at 1023 K (Fig. 4d). Under the latter conditions, the bands at 1100 and 450 cm^{-1} became broad and the absorption at 620 cm^{-1} was enhanced. The peak at 620 cm^{-1} was considered one of the characteristic absorptions of cristobalite (a low symmetry SiO_2) [17]. These results concordantly indicate the destruction of the ZSM-5 structure after Co-ZSM-5 was reduced at 1023 K, and are also consistent with the XRD measurement.

In comparison with the IR spectrum of ZSM-5 zeolite in the Si–O stretching vibration region, the unreduced Co-ZSM-5 sample has an extra shoulder at ca. 1028 cm^{-1}, which was retained after 793 K reduction. This 1028 cm^{-1} peak was also observed by Puskas et al. [13] in the silica supported cobalt system. It was assigned to authentic Co_2SiO_4. However, the presence of Co_2SiO_4 in Co-ZSM-5 zeolites is not likely because surface area data show no blockage of the zeolite pores. The 1028 cm^{-1} band is thus proposed due to cobalt substituted in zeolite framework. After reduction at 1023 K, the absorption in the Si–O stretching vibration region becomes very broad and two new peaks appear at ca. 900 and 935 cm^{-1}. The two new peaks are consistent with the strongest absorption observed in cobalt orthosilicate [17]. Therefore, it is proposed that some cobalt orthosilicate is formed during the high-temperature reduction process and that it is never being completely reduced.

Fig. 5a and 5b compare the XRD patterns of H-ZSM-5 before and after cobalt oxide being precipitated onto it. Both patterns are typical for ZSM-5, but the intensity for Co/ZSM-5 is apparently lower. Accordingly, the structure of ZSM-5 was somewhat damaged during the preparation procedure. In other words, cobalt ions reacted with the zeolitic framework in alkaline medium at 358–363 K. That also accounts for the decrease in surface area of Co/ZSM-5 as compared with that of pristine ZSM-5. After reduction at 793 K and 1023 K, both the structure and crystallinity of Co/ZSM-5 were found to be unchanged (Fig. 5c and 5d). These results are quite different from that observed on Co-ZSM-5, where the zeolite structure is seriously damaged after reduction at 1023 K. The corresponding IR spectra of Co/ZSM-5 reduced at different temperatures are shown in Fig. 6. Fig. 6a is that of Co/ZSM-5 calcined at 823 K and before reduction. The absorption at 665 cm^{-1} was very weak, indicating that there was only a very small amount of Co_3O_4 in the precipitated sample. In the Si–O stretching vibration region, a shoulder around 1028 cm^{-1} was also observed, although it is not as intense as that on Co-ZSM-5. That is also consistent with the results obtained from XRD and TPR experiments, which show that cobalt is mainly in some forms of cobalt silicate. After the sample was reduced at 793 K, its IR spectrum was virtually unchanged (Fig. 6b), but when the reduction temperature was raised to 1023 K, the small absorption at 665 cm^{-1} disappeared, the shoulder at 1028 cm^{-1} vanished, and the band at 1100 cm^{-1} became narrower (Fig. 6c). Actually, the spectrum is very similar to that of pristine ZSM-5. Accordingly, it is proposed that the cobalt atoms in Co/ZSM-5 are attached to the zeolite framework through bonding with two or three oxygen atoms. The assemblies may be in the form of (I) or (II)

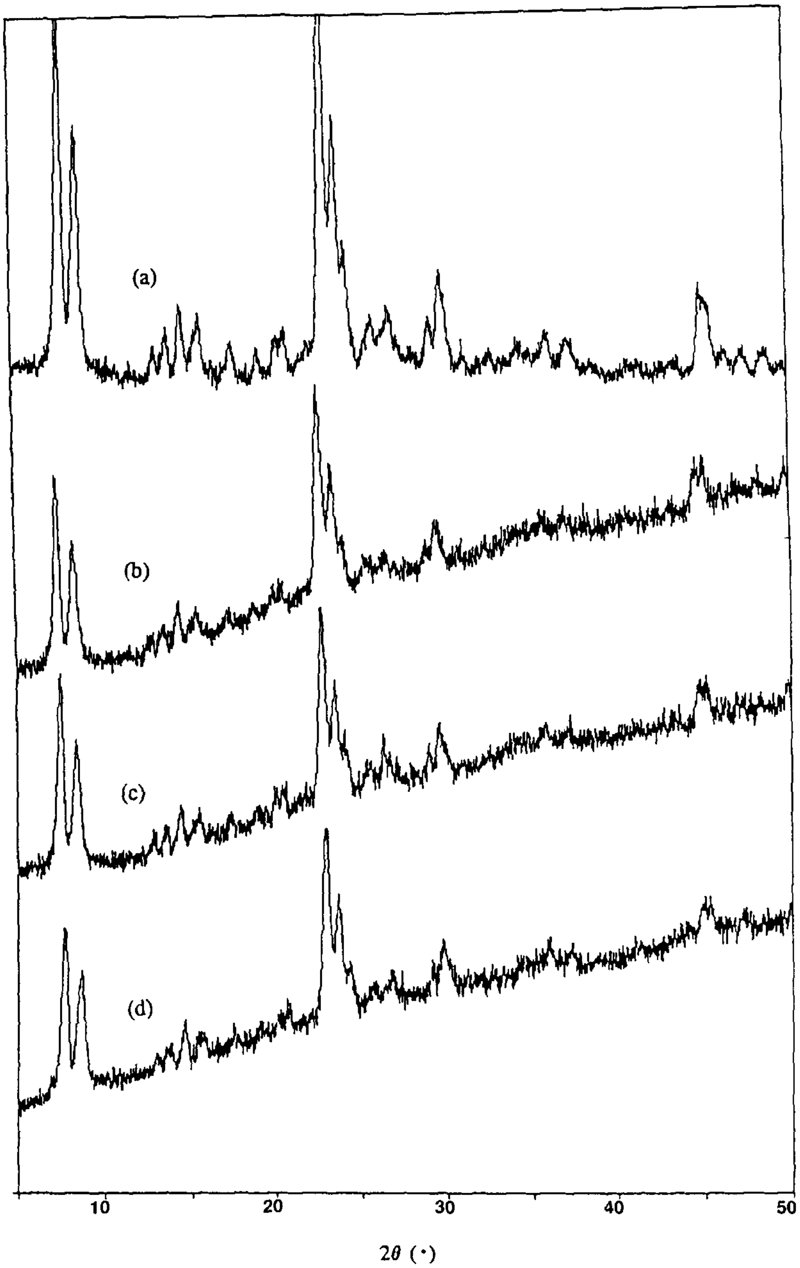


Fig. 5. XRD patterns of H-ZSM-5 (a); and Co/ZSM-5 before (b), and after reduction at 793 K (c) and 1023 K (d).

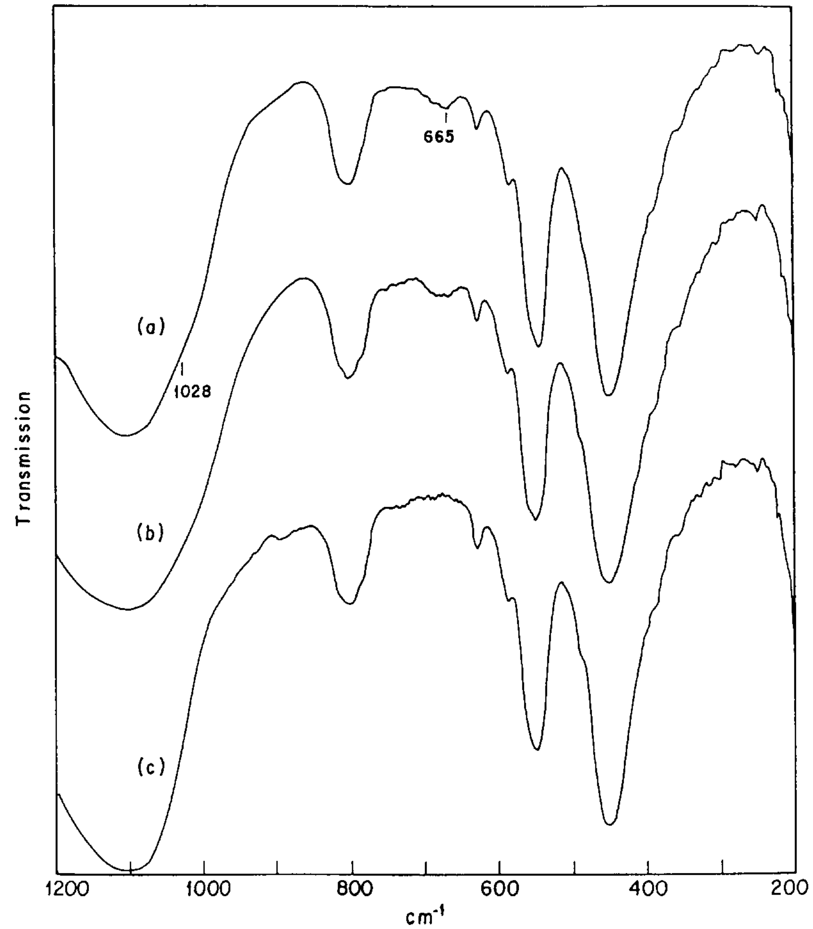
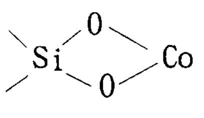
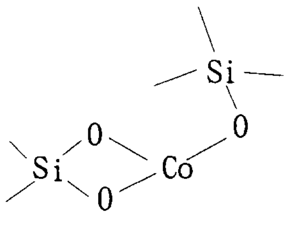


Fig. 6. IR spectra of Co/ZSM-5 before (a), and after reduction at 793 K (b) and 1023 K (c).



(I)



(II)

Their formation involves the break-down of portions of the zeolitic structure and their chemical properties are more like cobalt silicate than ion-exchanged cobalt. After reduction at 1023 K, cobalt was removed from these assemblies, and the zeolitic framework, which had been partially destroyed during impregnation, was retained.

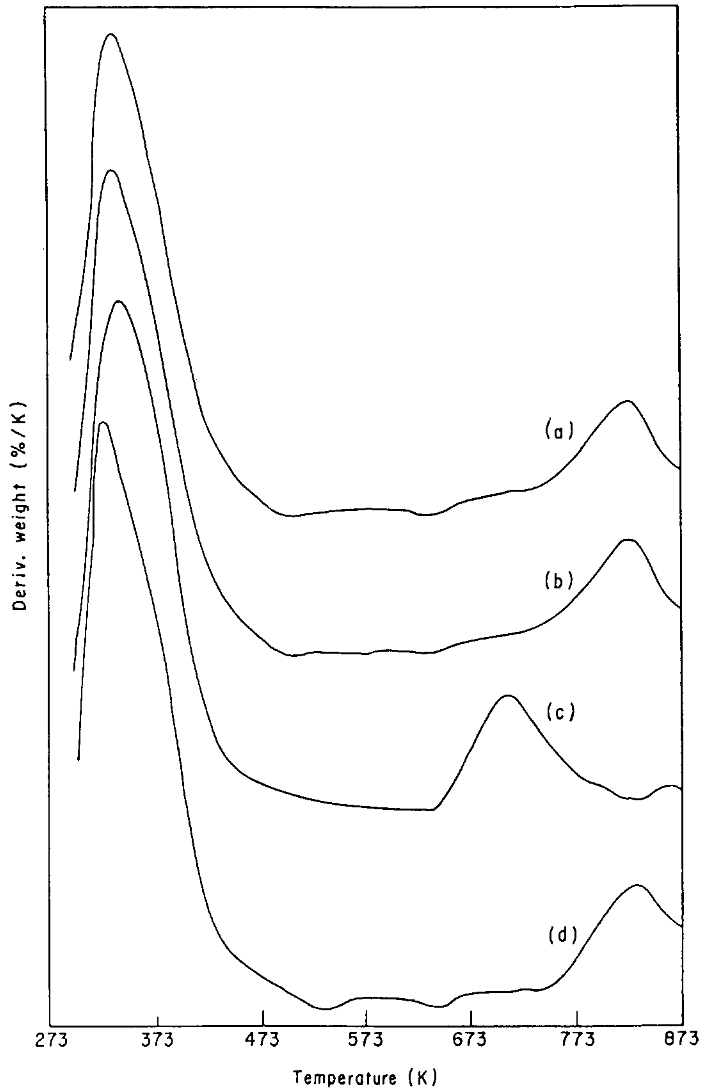


Fig. 7. TPD profiles of H-ZSM-5 (a), Co-ZSM-5 (Si/Co = 27) (b), Co-ZSM-5 (Si/Co = 5.4) (c), and Co/ZSM-5 (d).

The acidity of the catalysts was examined by carrying out temperature-programmed desorption of ammonia (Fig. 7). The desorption bands that appeared at temperatures lower than 473 K are attributed to physically adsorbed ammonia, and that at ca. 825 K is due to ammonia desorbed from the strongly acidic sites of ZSM-5. The TPD profile of Co/ZSM-5 is very similar to that of H-ZSM-5. In other words, the acidity of the sample was retained through the cobalt impregnation and H^+-re-exchange processes. On the other hand, Co-ZSM-5 with low cobalt content (Si/Co = 27) gives a similar TPR profile as that of H-ZSM-5. However, for Co-ZSM-5 with high cobalt content (Si/Co = 5.4), the desorption band was found to shift to lower temperature, ca. 710 K. Therefore, the latter catalyst has a lower

Table 3
Carbon monoxide hydrogenation over cobalt containing ZSM-5 zeolites

Catalysts	Co	Co/ZSM-5/PM	Co/ZSM-5	Co-ZSM-5	
Si/Co				(5.4)	(27)
CO conversion (mol-%)	93.6	94.0	3.6	41.9	0.7
Selectivity (mol-%)					
CH_n	64.1	64.5	91.5	64.4	88.5
CO_2	35.9	35.5	8.5	35.6	11.5
CH_n composition (wt.-%)					
C_1	59.2	62.6	48.9	40.3	51.3
C_2	9.9	9.0	22.9	5.2	21.4
C_3	5.4	9.6	15.1	9.0	12.8
C_4	5.4	6.8	4.3	7.8	1.8
C_{5+}	17.2	1.6	7.3	37.5	3.5
Aromatics	–	10.4	1.5	0.3	9.2
Wax	0.1	–	–	–	–
Gasoline range composition (wt.-%)					
C_5	24.8	18.1	31.5	16.5	8.1
C_6	17.1	8.2	13.0	19.2	4.8
C_7	15.8	2.1	11.5	17.8	14.6
C_{8+}	42.3	4.4	26.9	45.8	–
Benzene	–	3.7	0.3	–	3.0
Toluene	–	14.0	1.7	0.1	12.9
m,p-Xylene	–	14.8	10.8	0.3	42.0
o-Xylene	–	4.8	0.1	–	0.5
tmb[a]	–	14.6	0.4	0.3	–
Ethyltoluene	–	15.3	3.8	–	14.0

Reaction conditions: 300°C, 50 atm, $H_2/CO = 1$, 1 g catalyst, flow-rate: 20 cm^3/min.
[a] Trimethylbenzene.

acidity compared to the other three catalysts. On the other hand, there is no direct correlation between the acidity and the aluminum content in the zeolites.

The catalytic activities of the bifunctional catalysts, Co-ZSM-5 and Co/ZSM-5, in carbon monoxide hydrogenation were compared with that of a cobalt and ZSM-5 admixture (in 1:10 ratio, briefly termed as Co/ZSM-5/PM) as well as pure cobalt. Table 3 shows that the admixed catalyst has a higher carbon monoxide conversion than the catalysts prepared either by impregnating precipitation or coprecipitation. Because the TPR experiment shows that predominant cobalt species in the latter are not reducible under the reaction conditions, the low carbon monoxide conversion is attributed to the lower amount of metallic cobalt present in the catalysts. For Co-ZSM-5 of higher cobalt loading (Si/Co = 5.4), the presence of easily reduced extra-framework cobalt oxide is confirmed by the high carbon monoxide conversion.

The product distributions are very much different for catalysts from different preparation methods. Wax, which was detected on unsupported cobalt catalyst, vanished completely when ZSM-5 was added by any of the mentioned methods to form bifunctional catalysts. This result is ascribed to the shape selectivity and acidic function of ZSM-5. Aromatic products are remarkably enhanced when cobalt was physically mixed with H-ZSM-5. A similar enhancement in aromatics formation was observed over Co-ZSM-5 of low cobalt loading (Si/Co = 27), as the TPD of ammonia experiment shows that the acidity of the latter is similar to that of H-ZSM-5. As to Co-ZSM-5 of high cobalt loading (Si/Co = 5.4), which shows a lower acidity in TPD of ammonia, the aromatics selectivity is very low. Therefore, strong acid sites are responsible for the aromatics formation.

Although Co/ZSM-5 and Co-ZSM-5 (Si/Co = 27), both have a similarly low carbon monoxide conversion and high acidity, the hydrocarbon product distributions are very different. Over the former catalyst, the aromatics selectivity is low, and pentane is the main component of the liquid products (31.5%). The shift of liquid products towards lower molecular weight is attributed to the shape selectivity of the narrower pore windows in the zeolite, which is a result of the attachment of cobalt silicate-assemblies to the zeolite framework.

4. Conclusions

From the experimental results, it is concluded that cobalt can be highly dispersed in zeolite matrix either through incorporation of cobalt into the zeolite synthesis gel, or by precipitating cobalt oxide onto zeolite in alkaline solution. However, the resultant cobalt species are very different. From the structural characterization and TPR experiments, it was found that the main cobalt species in the co-precipitation catalysts (Co-ZSM-5) are cobalt substituted in ZSM-5 framework. Extra-framework Co_3O_4 also exists as minor component, and its content increases with cobalt loading. For the precipitating impregnation catalyst (Co/ZSM-5), cobalt silicate-like assemblies attached to the ZSM-5 framework were found to be the predominant cobalt species formed, and only negligible amounts of Co_3O_4 were present. While cobalt oxide is easily reduced below 793 K, framework cobalt and cobalt silicate assemblies need temperatures higher than 993 K to be reduced. Reduction of framework cobalt is accompanied with the destruction of the ZSM-5 lattice in Co-ZSM-5. However, the zeolitic structure is hardly affected through the reduction of cobalt silicate assemblies in Co/ZSM-5.

In carbon monoxide hydrogenation, only zero-valence cobalt is the active species. Because both Co-ZSM-5 (Si/Co = 27) and Co/ZSM-5 were hardly reduced under the pretreatment conditions, they showed low catalytic activities. Increasing the cobalt loading in Co-ZSM-5 increased the amount of reducible cobalt oxide in the catalyst. As a result, the conversion was increased, and non-aromatic gasoline range products became predominant. The low selectivity of aromatic products is attributed to the weaker acidity of the catalyst. In contrast, the physically admixed sample has the greatest amount of reducible Co_3O_4 and strong acidity from H-

ZSM-5; therefore it gives the highest activity as well as highest selectivity of aromatics products.

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