Comparison Studies of *in Situ* Loaded and Impregnated Silicalite-Cobalt Oxides

BEN-ZU WAN,* RAYFORD G. ANTHONY,* CARLOS SALDARRIAGA,† JAIME PEREZ,†
V. P. SHIRALKAR,† AND ABRAHAM CLEARFIELD†

*Kinetics, Catalysis and Reaction Engineering Laboratory, Department of Chemical Engineering, and
†Department of Chemistry, Texas A&M University, College Station, Texas 77843

Data are presented which strongly indicate that cobalt has been incorporated into the framework of silicalite. Experiments conducted to substantiate this claim are ion exchange, thermogravimetric, ammonia desorption, UV-visible spectrography, and catalytic activity for 2-propanol and hexane decomposition. Propylene is formed from 2-propanol for the hydrogen form of samples *in situ* loaded for cobalt compositions less than 4%. For hexane decomposition the reactions appear to be dehydrogenation of hexane to hexene and cracking of hexene to propylene followed by further decomposition to methane. The production of methane for samples with Co greater than 1% is high. However, the active sites for the *in situ* loaded catalyst are very difficult to reduce and appear to be different than the impregnated Co samples. © 1991 Academic Press, Inc.

INTRODUCTION

The ZSM-5 family of molecular sieves consists of an essentially silica framework containing up to 3% of aluminum substitutions. The pore structure of these zeolites is defined by 10-membered ring apertures which are nearly circular or elliptical and form an intricate channel system (*1, 2*). The unique attractiveness of pentasil zeolites as catalysts is twofold: First, they possess shape-selective characteristics that discriminate between many molecules of interest based on steric factors; and second, they can be produced with a range of intrinsic activities by systematically varying the Al content (*3*). Protons associated with the aluminum sites exhibit strong Brønsted acidity. This high acidity tends to reduce catalytic selectivity especially for reactions which do not require strong acid sites (*4*). In view of this limitation, many attempts to modify the acidity by substitution of metals other than aluminum into the ZSM-5 framework have been carried out.

Kotasthane *et al.* (*4*) have investigated the possibility of isomorphous substitution of Fe while Chu and co-workers (*5*) examined boron substitution in ZSM-5. Szostak *et al.* (*6*) have reported on Fe-, and Cr-containing forms of ZSM-5 while a patent has been issued (*7*) for Ni and Zn substituted silicalite. A mixed Al, Co-containing phase has also been the subject of a patent (*8*). Very recently excellent evidence has been deduced for incorporation of Co^{2+} into the ZSM-5 framework from XPS and electron microprobe analysis (*9*). The zeolites were synthesized by first preparing a cobalt containing amorphous dried gel and incorporating this into the final synthesis mixture.

One of the objectives of the cited studies, was the determination of whether there is a variation in acidity and catalytic properties in the framework substituted products. This has not been resolved in a convincing fashion. In studies reported here, cobalt with no external aluminum addition has been incorporated into the silicalite framework. By excluding aluminum from the preparation, catalysts could be studied without interferences which would be caused by the presence of acid sites produced by framework aluminum. The physi-

458

cal and catalytic properties of the Co^{2+} substituted catalysts and a catalyst in which cobalt oxide has been impregnated on the silicalite surface have been compared. X-ray powder diffraction, BET surface areas, temperature-programmed NH_3 desorptions, ion exchange, and catalytic activity for 2-propanol decomposition and hexane cracking in a pulse reactor, have been utilized in the comparison. The resistance to reduction by H_2 of these two series of catalysts was also explored. The objectives of this paper are to (1) provide evidence that cobalt is isomorphously substituted into the framework of silicalite catalysts; (2) explore new acidic sites; and (3) compare the catalytic properties of cobalt substituted ZSM-5 with Co^{2+} impregnated on silicalite.

TABLE 1

Elemental Analysis and BET Surface Areas of in Situ Loaded ZSM-5 (HSiCo-*x*) and Silicalite Impregnated with Co (II)

	Sample	Si/Co in reactant mix	Co (wt%)	Al (wt%)	BET Surface area (m²/g)
	ZSM-5[a]	—	—	1.50	377
	Silicalite	—	—	0.11	329
Framework substituted samples	HSiCo-1	20	5.1	0.051	—
	HSiCo-8	40	4.70	0.084	393
	HSiCo-9	80	0.80	0.098	432
	HSiCo-10	160	0.53	0.140	432
	HSiCo-15	60	1.48	—	412
Impregnated samples	ISiCo-2		0.85	0.089	383
	ISiCo-4		2.99	0.164	328
	ISiCo-5		7.96	0.104	326
	ISiCo-6		0.04	0.15	322

[a] Prepared by R. Szostak, Engineering Experiment Station, Georgia Institute of Technology.

EXPERIMENTAL

Preparations

Synthesis of in situ loaded Co-silicalite. A solution prepared with 1.4 g of $CoSO_4 \cdot 7H_2O$ in 40 g of water was first added to 60.0 g of Ludox HS-40 colloidal silica and the blue gel obtained was stirred until homogeneous. Then, two solutions were prepared separately; one containing 8.0 g of tetrapropylammonium bromide (TPABr) in 40 ml of water, and the other containing 8.0 g of sodium hydroxide in 66 ml of water. These solutions were added simultaneously to the above blue gel. A final bluish-green reaction mixture was obtained of composition $3(TPA)_2O : 20Na_2O : CoO : 80SiO_2 : 2029H_2O$, which was further stirred until homogeneous. The mixture was then sealed in a wide-mouth polypropylene bottle of 500-ml capacity and heated at 100°C for 88 h. A light-brown crystalline solid, possessing an MFI-type of structure, as demonstrated by its X-ray powder pattern (Table 2), was recovered by filtration and was subsequently washed with water and dried at 100°C. This sample is labeled SiCo-9.

All the samples listed in Table 1 were prepared in the same manner except that the Si/Co ratio was varied from 160 to 20.

At the same time, the ratio of SiO_2 to NaOH was fixed at 2 and the ratio of SiO_2 to TPABr was 13.33, while H_2O/Si was kept constant at a value of 25.5. After crystallization and washing with water, the solids were calcined above 673 K for 2 h and then at 783 K for 2 h in air. Ammonium ion exchange with these calcined samples were performed in solution with 1 M NH_4Cl at 363 K three successive times. The samples were dried at room temperature after each exchange treatment. After exchange, the samples were heated at 673 K overnight and at 773 K for 2 h in air. Samples so treated are designated as HSiCo—followed by a number (Table 1).

Cobalt impregnated samples. The impregnated samples were prepared by stirring together $Co(OOCCH_3)_2 \cdot 4H_2O$ and 6 g of silicalite, made in this laboratory, in 50 ml of deionized water at 363 K for 2 h. After filtration and drying in air, they were heated at 773 K for 3 h., then 803 K for 8 h. The different loadings of cobalt on these impregnated samples were prepared by changing the initial concentration of $Co(OOCCH_3)_2 \cdot 4H_2O$ in the solution. The silicalite was subjected to NH_4^+ exchange

three times followed by calcination before it was used for impregnation. These samples are designated I SiCo—followed by a number.

Apparatus and Procedures

The apparatus and procedures for carrying out X-ray powder diffraction, BET surface area measurements, and temperature-programmed desorption (TPD) of NH_3 were the same as those described in Refs. (10, 11), except that the temperature for TPD of NH_3 was increased at the rate of 10°C/min with a sweep gas (helium) flow rate of 60 ml/min. The amount of each sample used for TPD was about 0.5 g; and before the adsorption of ammonia at room temperature the samples were degassed at 723 K overnight, then at 773 K for 2 h under helium.

Reactions were conducted in a $\frac{3}{8}$-in. stainless-steel (type 316) pulse reactor at a total pressure of 18 psig. Prior to reaction the catalyst, about 0.17 g, was heated in a flow of helium at 773 K overnight, and then at 823 K for 2 h. Hexane or 2-propanol was fed by passing a helium stream through a saturator at 298 K. The total volume of each pulse was 0.38 ml. Blank runs without catalysts and with hexane feed were conducted at frequent intervals throughout the experimental program to ensure that the reactor walls had not been activated. Further details on the reactor system and catalytic procedures have been previously described (10).

Elemental analysis for cobalt and aluminum in each sample was carried out by Inductively Coupled Plasma (ICP) Methods in the Department of Chemistry at Texas A&M University while a combination of AA, ICP, TGA, and C, H, N analysis was utilized for the complete elemental analysis of the template containing precursor for sample HSiCo-1. Found were Co, 4.99%; Si, 33%; Al, 0.051%; Na, 2.4%; C, 9.55%; N, 0.95%; H, 2.5%. This analysis corresponds to the formula 0.78 TPA: 0.6 Na_2O: CoO: 13.8 SiO_2: 5.1 H_2O which requires

5.00% Co, 32.9% Si, 2.34% Na, 9.54% C, 0.93% N, 2.8% H.

RESULTS

Catalyst Characterization

All of the impregnated samples were pink in color while all those in which Co^{2+} was added to the gel were brown in color. In the completely analyzed template containing precursor to HSiCo-1, the Si : Co ratio was 13.8 as compared to 20 in the reactant mix. Thus, a portion of the silica must have remained dissolved in the NaOH solution. Analytical data for the experimental samples are collected in Table 1. A small amount of aluminum, which must derive from the original Ludox gel employed, was always present in the products. Figure 1 presents the thermogravimetric curves for the template-containing precursor (curve 1) and the calcined (520°C) product after saturation with water and air drying (curve 2). The calcined products were gray in color.
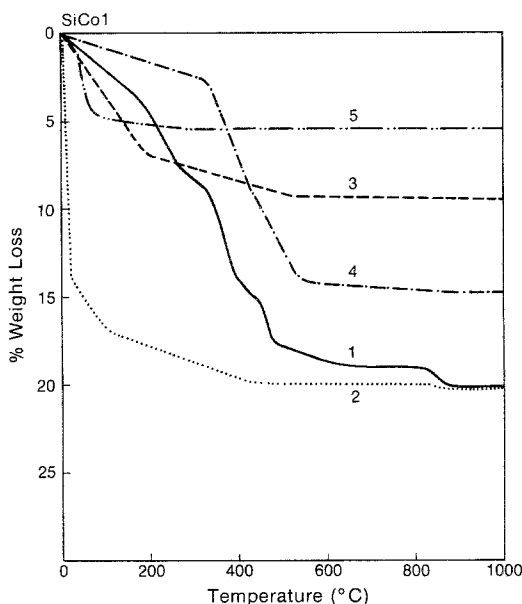

FIG. 1. TGA curves for the precursor (curve 1), calcined and saturated with water (curve 2), and NH_4^+-exchanged (curve 3) forms of SiCo1 as compared to that for the precursor to silicalite (curve 4) and its calcined form after saturating with water and drying in the air at room temperature (curve 5).
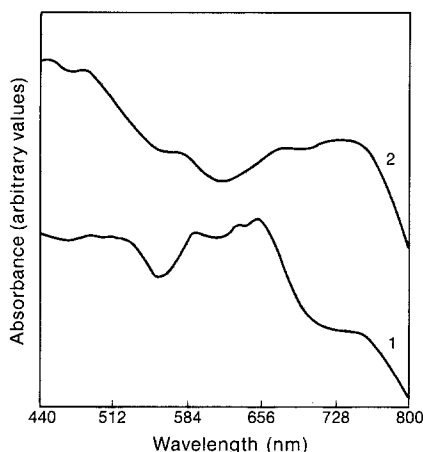
FIG. 2. UV-visible spectra of SiCo1. Curve 1: Calcined form (520°C m, 2 h, gray solid). Curve 2. NH$_4^+$ form heated to 1000°C (light-brown solid).

Curve 1 shows a loss of approximately 7.0% water below 250°C and about 12% additional weight loss to 800°C. A final 1% weight loss was observed to occur at slightly above 800°C. This may be due to the final removal of water from protons required to balance the charge. It should be noted that somewhat less than the required amount of sodium ion was present in the solid sample SiCo-1. However, after removal of the template, the solid was exchanged exhaustively with Na$^+$, washed and then treated three times with 1 M NH$_4$Cl at 65°C to completely replace the Na$^+$ by NH$_4^+$. The amount of Na$^+$ recovered was 2.0 meq/g of dry exchanger (MW = 926) as compared to a theoretical exchange capacity of 2.15 meq/g.

Reference to curve 3 in Fig. 1 shows that the ammonium ion form of SiCo-1 yields a total weight loss of 9.4% in two steps. The first step is probably water removal and amounts to 6.5% while the second step is largely due to loss of NH$_3$. These values correspond to 3.7 moles of H$_2$O and 1.74 moles of NH$_3$.

The weight loss results may now be compared to silicalite itself. Curve 4 in Fig. 1 shows a water loss of 2.5% and a template

content of 12%. Thus, the silicalite contained less water than TPA-SiCo-1, but a similar amount of template. However, the hydrophobic character of silicalite is shown by the fact that after removal of the template and saturation with water, it contained only 5.5% H$_2$O. This compares to 20% for HSiCo-1 (curve 2).

An interesting sidelight to these heating experiments is the fact that the synthesized solid containing the template formed cristobalite on heating to 1000°C, whereas the ammonium ion phase retained the ZSM-5 structure under similar treatment.

UV-visible spectra for NaSiCo-1 heated to 520°C to remove the template and HSiCo-1 (NH$_4$SiCo-1 heated to 1000°C) are shown in Fig. 2. Curve 1 contains three major absorbances at 526, 592, and 639 nm. This compares to values of 532, 590, and 639 nm for Co^{2+} in the mineral busakite (*12*) where the cobalt is in tetrahedral oxygen coordination in the framework. On heating the ammonium ion form to 1000°C, a shift to lower wavelength occurs and the absorption bands are now at 488, 515, and 577 nm. While a shift to lower wavelengths may indicate the presence of some octahedrally coordinated Co^{2+}, the high absorbance indicates that this is not the case. Rather the Co–O bond distance may decrease on heating with concomitant increase in the crystal field splitting energy.

The temperature-programmed ammonia desorption profiles of HSiCo-8, HSiCo-9, ISiCo-2, silicalite, and ZSM-5 (with 1.5 wt% Al, Table 1) are shown in Fig. 3. The desorption temperature was varied from 300 K to 773 K with ammonia initially sorbed at 298 K.

For HSiCo-8, maximums occurred in the TPD profile at 400 and 430 K. The shoulder around 360 K is probably due to physical desorption of ammonia. Furthermore, above 430 K, weak desorption bands—between 450 and 550 K—are observed. The TPD of NH$_3$ of HSiCo-8 which had been treated with ultrahigh purity hydrogen at 30 ml/min at 783 K for 2 h *in situ* was also
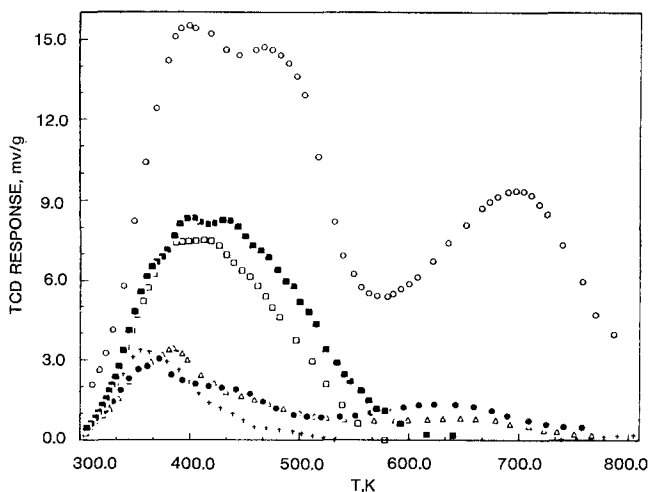
FIG. 3. TPD of ammonia on HZSM-5 and cobalt silicalite catalysts (○) HZSM-5, (■) HSiCo-8, (□) reduced HSiCo-8, (△) ISiCo-2, (●) HSiCo-9, (+) silicalite.

investigated. The maximum in the TPD profile, shown in Fig. 3, shifted by about 10 K to a lower temperature, and the dual hump was eliminated.

The desorption curves from HSiCo-9, ISiCo-2, and silicalite were much less intense than that of HSiCo-8. However, for both ISiCo-2 and HSiCo-9, distinct broad peaks around 650 K were found. A maximum peak around 390 K for ISiCo-2, and a small band ranging from 400 K to 440 K for HSiCo-9 were also observed. For silicalite, the main desorption peak, as shown in Fig. 3, is around 363 K which is from physical desorption. Above 750 K, a desorption band seems to start to grow; however, the desorption of ammonia at temperatures above 800 K was not investigated in this study.

The TPD curve of ammonia from HZSM-5, shown in Fig. 3, indicates that there are two weak acid sites, one is at a desorption temperature of 400 K, another is at approximately 480 K; also, a strong acid site can be observed with a maximum at 700 K. Topsøe et al. (13) have interpreted their desorption bands from HZSM-5 as representative of Brønsted and Lewis sites, respectively. The large number of sites for

HZSM-5 as compared to the Co–Si samples is probably due to the very strong acidity of Al^{3+} as compared to Co^{2+}. On a mole basis the ratio $Co^{2+}:Al^{3+}$ for HSiCo-8 and HZSM-5 is 1.44. Thus, the higher ammonia uptake should have been recorded by HSiCo-8. However, as we shall see the acidity of the cobalt samples is much less than that of HZSM-5, based upon the catalysis studies.

Catalytic Activity

2-propanol decomposition. The *in situ* loaded catalysts (HSiCo-J, J = 1, 8, 9, and 15) listed in Table 1 were evaluated for the activity of converting 2-propanol to propylene or acetone. Production of propylene and hydrocarbons formed by secondary reactions indicates the presence of acidic sites on the catalyst. Whereas production of acetone indicates basic sites. At 473 K, an apparent residence time of 0.43 mg/ml/min (residence time of approximately 0.026 s) and 224 kPa, 2-propanol conversion was 100%, and propylene was obtained for all of the catalysts, except for HSiCo-1.

Decomposition of 2-propanol over HSiCo-1 was low and yielded a mixture of acetone and propylene indicating the pres-
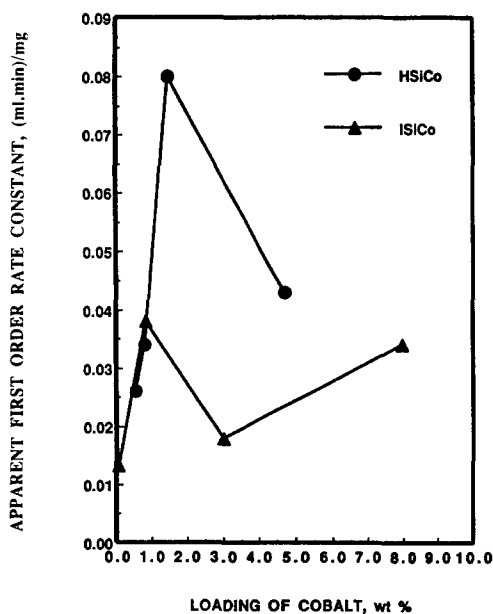
FIG. 4. Catalytic activity for hexane decomposition on HSiCo and ISiCo catalysts.

ence of acidic and basic sites. At 473 K, the rate constants were 0.0064 ml/min/mg and 0.0128 ml/min/mg for dehydration and dehydrogenation, respectively. For the temperature range of 472 to 540 K, the activation energies were 26 and 21 kcal/mol for dehydration and dehydrogenation, respectively. As the temperature increases the activity for dehydration with acidic sites increases faster than the activity for dehydrogenation. This result is surprising, for dehydrogenation of 2-propanol usually has a higher activation energy than 2-propanol dehydration. Because this catalyst clearly has the dehydrogenation function which indicates the presence of cobalt oxide in the channel, and because of its low surface area, no further work was performed with HSiCo-1.

Hexane decomposition. Figures 4 and 5 illustrate the activity for hexane decomposition by expressing the rate data for both types of catalysts in terms of apparent first-order rate constants. The results indicate that the activities of the Co^{2+} *in situ* loaded samples are independent of the aluminum

content and attain a maximum at a loading close to 1.48% Co. In contrast the silicalite samples impregnated with Co^{2+} exhibited lower rates at cobalt loadings greater than 1%. Apparent activation energies of these catalysts, 21K cal/mol for HSiCo-9, 23K cal/mol for HSiCo-10, and 25K cal/mol for both ISiCo-2 and ISiCo-6, are within a close range.

The conversion and product distribution for hexane decomposition over each catalyst at a reaction temperature of 723 K, apparent residence time of 5.19 mg/mol/min and reactor pressure of 225 kPa are shown in Table 3 and Fig. 6. The apparent residence time is defined as weight of catalyst (mg) divided by the volumetric flow rate (ml/min) calculated at reaction conditions of the helium carrier gas. Dehydrogenation of hexane followed by decomposition of hexene is clearly occurring on the impregnated and *in situ* loaded samples. At low cobalt loadings there appears to be some acidic type of cracking activity in addition to the formation of methane. Figure 6 illustrates the similarities of the catalysts. Only a single curve can be drawn through the points for the propylene content. Two
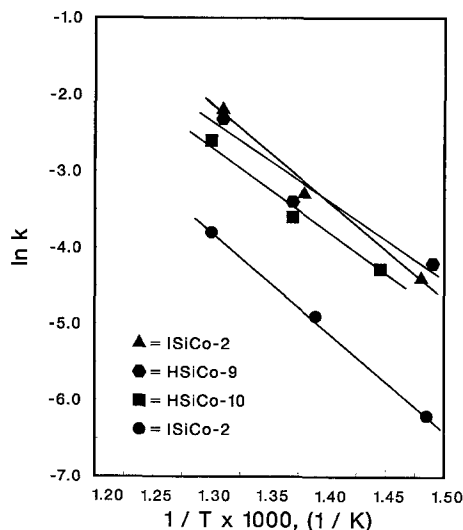

FIG. 5. Arrhenius plots for hexane decomposition on HSiCo and ISiCo catalysts.
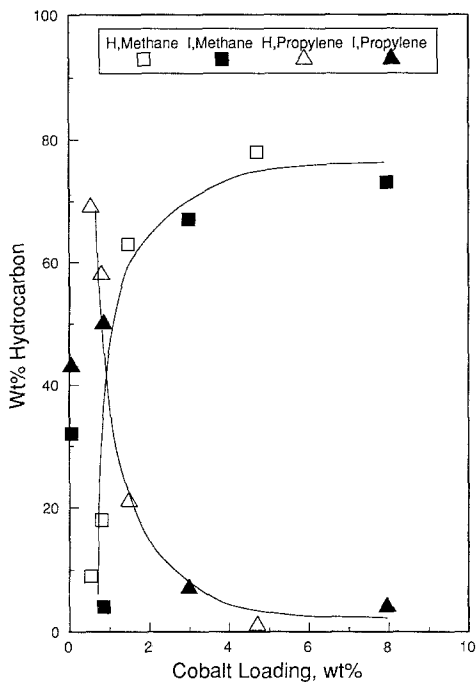
FIG. 6. Effect of cobalt content on product distribution. Open points are for *in situ* loaded samples, and closed points are for impregnated samples.

curves might be used for the methane content, but allowing for experimental error, and without more data this is not at all certain. However, for benzene production (Table 3) there does seem to be a difference in the performance of the *in situ* loaded versus the impregnated catalysts, with the *in situ* loaded catalyst indicating more acidic type of activity since the benzene content is low.

To further distinguish the two types of catalysts, HSiCo-9 and ISiCo-2, with Co loadings of 0.80% and 0.85%, respectively, were treated with oxygen and hydrogen at 839 K. The impregnated catalyst, ISiCo-2, on additional oxygen treatment showed an increase in the methane content and a small decrease in propylene. Activity was slightly greater than the initial catalyst. After reduction with hydrogen, a significant increase in methane production occurred due to the formation of Co⁰ produced in the reduction step (*14*).

For the HSiCo-9, hydrogen treatment re-

sulted in a decrease in methane, and increases in propane and C₄'s. With further treatment with oxygen and hydrogen, the activity decreased and the methane content was 24% as compared to the methane content of 18% produced prior to the hydrogen, oxygen, hydrogen treatment. These data strongly indicate that a different active site, probably an acidic site is present on the *in situ* loaded Co samples at low loadings. The cobalt in HSiCo-9 appears to be incorporated within the framework, because cobalt in the channels should have been readily reduced as was the impregnated samples with a correspondingly large increase of methane in the products.
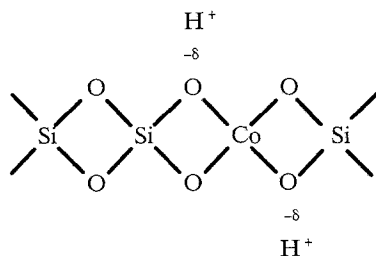
DISCUSSION

In this study we have presented evidence for the incorporation of Co^{2+} into the framework of silicalite. This evidence includes the appearance of ion exchange sites, temperature-programmed ammonia desorption, UV-visible spectra and the general catalytic behavior toward 2-propanol decomposition and hexane decomposition. It should be remembered that the hydrothermal synthesis was carried out at 100°C. This procedure produces a brown colored product, the same color reported by Rossin *et al.* (*9*). When the hydrothermal procedure was attempted at temperatures of 150–190°C, a pink product indicative of 6-coordinate cobalt, was always obtained.

Incorporation of the larger Co^{2+} ion ($r_{Co^{2+}} = 0.72$ Å, $r_{Si^{4+}} = 0.41$ Å) into the framework would be expected to increase the unit cell dimensions over those of pure silicalite. However, the crystallinity of the products prepared at 100°C were relatively poor and although the X-ray pattern was similar to that of ZSM-5 (Table 2), the highly accurate cell dimensions required could not be obtained from these X-ray patterns. In fact the low crystallinity and long reaction times of the preparations, described here, led Saldarriaga to initiate the precursor gel studies (*9*) while still present in our laboratory.

The studies of TPD of ammonia have

provided strong evidence that cobalt is incorporated into the framework of the silicalite catalysts. The TPD of ammonia from HSiCo-8, as shown in Fig. 2, indicates two new desorption bands at 400 K and 430 K, which may correspond to two new weak Brønsted acid sites. Strong acid sites are also exhibited for the samples with low cobalt loadings, with the incorporated cobalt sample HSiCo-9 having a somewhat greater number of strong acid sites than the impregnated sample ISiCo-2. For a similar study of boron isomorphously substituted into the framework of ZSM-5, a new desorption band at 440 K for TPD of ammonia has been reported (5). Also, new acidic sites are expected for the catalysts with a metal oxide in the framework of the silicalite. The catalytic activity for decomposition of 2-propanol to propylene on all of the incorporated catalysts may be due to these weak acid sites. The new acidic sites created by cobalt may be as illustrated in Scheme I.

TABLE 2

X-Ray Powder Diffraction Data for HSiCo-9

$d(\text{Å})$	I^*
10.78	Offscale
9.72	70
6.56	9
6.24	11
5.87	18
5.57	10
5.47	12
4.93	7
4.53	5
4.29	7
4.19	9
3.80	54
3.68	34
3.58	12
3.40	7
3.27	8
3.01	6
2.96	13
2.94	7

H^+

$-\delta$

Si — O — Si — O — Co — O — Si

$-\delta$

H^+

SCHEME I. New acidic sites.

Reduced cobalt oxide with a hydrogenolysis property has been reported by Machiels and Anderson (14, 15). This property is attributed to strong resistance to desorption of cracking reactants. In our studies, shown in Table 4, similar results were also observed for the reduced impregnated catalyst. ISiCo-2, having cobalt oxide impregnated in silicalite, was found to change to a strong hydrogenolysis catalyst after being reduced by hydrogen at 839 K for 12 h. However, completely different results were observed for the *in situ* loaded catalyst. HSiCo-9, in which cobalt oxide is *in situ* loaded retained its initial characteristics after the hydrogen treatment.

The effect of hydrogen treatment at high temperatures on cobalt *in situ* loaded catalysts presented in Table 4 provides evidence that cobalt is in the framework of the silicalite, since the *in situ* prepared catalyst HSiCo-9 exhibited greater resistance to reduction by hydrogen than cobalt oxide impregnated onto the silicalite (ICoSi-2). Only after oxygen treatment at 839 K followed by reduction with hydrogen at 839 K was the product distribution changed, i.e., reduced propylene and increased methane content. This treatment should have resulted in extraction of some of the cobalt from the framework.

The studies of hexane decomposition show that low cobalt loading (lower than 0.85%), whether in cobalt *in situ* loaded or cobalt oxide impregnated catalysts, have similar catalytic properties and similar active sites. The data presented in Figs. 4, 5, and 6, and Tables 3 and 4 show that for similar low loadings of cobalt in both series of catalysts (HSiCo-9 and ISiCo-2), similar total conversions, apparent first-order rate constants, product distributions, and ap-

TABLE 3

Conversion of n-Hexane

$T = 723$ K, pressure $= 18$ psig, and apparent residence time $= 5.19$ mg/ml/min

Catalyst	Wt% of Co	% Conversion	k^a	Product distributions (wt%)								
				C_1	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	C_B^b	C_6^+
HSiCo-8	4.7	20	0.043	78	1	—	1	—	—	—	15	6
HSiCo-15	1.48	34	0.080	63	2	2	21	4	4	—	1	4
HSiCo-9	0.8	16	0.034	18	4	1	58	3	11	2	2	Trace
HSiCo-10	0.53	13	0.027	9	6	2	69	Trace	10	Trace	3	Trace
ISiCo-5	7.96	16	0.033	73	2	—	4	—	Trace	3	16	2
ISiCo-4	2.99	8.7	0.0176	67	2	—	7	—	1	3	10	10
ISiCo-2	0.85	18	0.038	4	5	4	50	2	10	3	9	13
ISiCo-6	0.04	6.7	0.013	32	4	2	43	1	11	5	2	—
HSi-8^c	0	2.7	0.0026	12	6	11	33	14	24	—	Trace	—
Silicalite^{c,d}	0	3.7	0.0036	39	6	7	39	Trace	10	—	Trace	—
ZSM-5	0	76	0.28	4	13	6	17	33	18	3	1	6

^{a} The k value reported is an apparent rate constant for hexane decomposition, ml/(mg min).

^{b} C_B is benzene.

^{c} The apparent residence time with silicalite and HSi-8 is 10.67 mg/ml/min.

^{d} This sample was obtained from Union Carbide. HSi-8 was prepared in our laboratories, and contained less Al than the Union Carbide silicalite.

parent activation energies are obtained. The apparent activation energies for hexane decomposition of 21 and 25 Kcal/mol when using HSiCo-9 and ISiCo-2 are significantly lower than the activation energies ($\sim$30 Kcal/mol) obtained with silicalite and with zeolites with aluminum in the framework (16). The activities of these cobalt

TABLE 4

Influence of O_2 and H_2 Treatment of HSiCo-9 and ISiCo-2 on Hexane Decomposition

Catalyst	Treatment	% Conversion	k^a	Product distributions (wt%)								
				C_1	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	C_B^b	C_6^+
ISiCo-2 (0.85% Co)		18	0.038	4	5	4	50	2	10	3	9	13
	O_2 for 12 h then	20	0.043	17	5	1	47	3	12	1	8	6
	H_2 for 12 h	25	0.055	75	Trace	—	3	—	Trace	—	15	7
HSiCo-9 (0.8% Co)		16	0.034	18	4	1	58	2	11	2	2	Trace
	H_2 for 10 h then	19	0.041	5	7	4	58	7	13	3	3	—
	H_2 for 12 h then O_2 for 12 h then	18	0.031	6	7	5	53	5	12	3	2	7
	H_2 for 6 h	13	0.027	24	4	3	41	10	9	Trace	4	4

Note. Reaction temperature $= 723$ K. Apparent residence time $= 5.19$ mg/ml/min. O_2 and H_2 treatment temperature $= 839$ K. Flow rate of O_2 and $H_2 = 30$ ml/min.

^{a} k has units of (ml)/(mg min.)

^{b} C_B is for benzene.

catalysts appear to be independent of the Al content which is present as an impurity in the reagents used to prepare the catalyst.

CONCLUSIONS

Evidence has been presented which strongly indicates that cobalt has been incorporated into the framework of a cobalt silicalite catalyst. The strongest evidence is the existence of ion exchange capacity and an increase in the hydrophillic character of the silicalite with the *in situ* loaded cobalt. The UV-visible spectra also show bands indicating that the cobalt is in a tetrahedral coordination as opposed to the octahedral coordination in cobalt oxide. The TPD of ammonia indicates the presence of new acidic bands and an adsorption capacity for ammonia greater than silicalite. The 2-propanol and hexane decomposition reactions illustrate the existence of acidic sites which would be present if cobalt is in the framework. Even though the impregnated catalyst and the incorporated catalyst show similar dehydrogenation and cracking characteristics in Fig. 6, the additional experiments illustrated in Table 4 provide strong evidence that the active sites in the *in situ* loaded cobalt silicalite are different than the active sites in the impregnated catalyst. The higher activity of the *in situ*-loaded cobalt silicalite catalyst also support the existence of a different type of active site. All of these results strongly indicate that cobalt has been incorporated into the framework of silicalite. They also show that even though incorporation has occurred some of the cobalt may remain in the channels, or can be extracted with severe treatment.

This would be particularly true for the samples with the higher cobalt content.

REFERENCES

1. Kokotailo, G. T., Lawton, S. L., Olson, D. H., and Meier, W. M., *Nature (London)* **272**, 437 (1978).
2. Pluth, J. J., and Smith, J. V., *Amer. Chem. Soc. Sympos. Ser.* **218**, 119 (1983).
3. Haag, W. O., *Proc. Int. Zeolite Conf.* **6**, 466 (1983).
4. Kotasthane, A. N., Shiralkar, V. P., Kullkarni, S. B., *Zeolites* **6**, 253 (1986).
5. Chu, C. T-W., Kuehl, G. H., Lago, R. M., and Chang, C. D., *J. Catal.* **93**, 451 (1985).
6. Szostak, R. M., Simmons, D. K., Nair, V., and Thomas, T. L., Ferrosilicate and Modified Ferrosilicate Molecular Sieves, B-10, *in* "9th North Amer. Mtg. The Catalysis Soc., Houston, Tx, March 1985."
7. Dwyer, T. G., and Jenkins, E. E., U. S. Pat. 3,941,871.
8. Petrine, B. P., U. S. Patent 4, 100, 262.
9. Rossin, J. A., Saldarriaga, C., and Davis, M. E., *Zeolites* **7**, 295 (1987).
10. Wan, B-Z., Ph.D. dissertation, Texas A&M University, 1986.
11. Wan, B-Z., Anthony, R. G., Peng, G. Z., and Clearfield, A., *J. Catal.* **101**, 19 (1986).
12. Burns, R. G., "Mineralogical Applications of Crystal Field Theory," p. 61. Cambridge U. Press, Cambridge, 1970.
13. Topsøe, N-Y., Pederson, K., and Derouane, E. G., *J. Catal.* **70**, 41 (1981).
14. Michiels, C. J., and Anderson, R. B., *J. Catal.* **58**, 253 (1979).
15. Michiels, C. J., and Anderson, R. B., *J. Catal.* **58**, 260 (1979).
16. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6**, 278 (1966).