AROMATIZATION OF PROPANE OVER Zn/HZSM-5 CATALYSTS PREPARED BY CHEMICAL VAPOR DEPOSITION

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Abstract - Zinc was introduced into HZSM-5 by chemical vapor deposition (CVD) to investigate the catalytic properties of Zn/HZSM-5 for propane conversion. Irrespective of catalytic precursor or ion exchange method, protons were found to be replaced by Zn ions. However, Zn species in the zeolite were different depending on the precursors used. Although the addition of Zn decreased the intensity of the Brønsted acidity, it did not caused the apparent formation of Lewis acid sites unlike Ga/HZSM-5 catalysts. On Zn/HZSM-5, both Zn and protons intervene in propane activation step.

INTRODUCTION

The addition of a catalytic (de)hydrogenating function, e.g., Ga or Zn to HZSM-5 is known to significantly enhance the activity and/or selectivity to aromatics for the aromatization of light paraffins [Csicsery, 1970; Gnep et al., 1988, Inui and Okazumi, 1984; Le Van Mao et al., 1990; Meriaudeau and Naccache, 1989; Mole et al., 1985]. Among these additives, Ga has been most extensively studied because of its superior selectivity to aromatics and the high stability of Ga/HZSM-5. The catalytic performance of Zn in HZSM-5 is comparable to that of Ga but Zn is less stable due to the high vapor pressure of Zn^0 [Seddon, 1990]. The problem of Zn volatilization can, however, be alleviated by alloying Zn with Cu [Chu, 1978; Planck et al., 1979], Ni [Planck et al., 1979], Ga [Chu and Chester, 1983] or Pd [Chu and Chester, 1983].

For the preparation of Zn/HZSM-5 catalysts, several methods such as aqueous ion exchange [Mole et al., 1985], physical mixing [Kanai and Kawata, 1988; Le Van Mao, 1990; Yao et al., 1990] and sublimation of $ZnCl_2$ or ZnO [Guisnet et al., 1991; Yang et al., 1989] have been used. All these catalysts show a similar catalytic behavior, but a few questions remain open:

1. No consensus exists on the acidic properties of Zn/HZSM-5. Yang et al. [1989] showed for a physical mixture of ZnO and HZSM-5 that the acidity decreased after heating at 580°C for 1 h, but Kanai and Kawata [1988] observed no change in acidity. Some published results show that when ZnO is sublimed into HZSM-5, Zn is incorporated into the ion exchange positions of the zeolite [Yang et al., 1989]. In contrast, it has been claimed that $ZnCl_2$ does not replace zeolite cations [Guisnet et al., 1988]. This is surprising in view of our pre-

vious findings with $GaCl_3$ [Kwak and Sachtler, 1993]; in that case Ga is positioned as $(GaO)^+$ in ion exchange positions of the zeolite. It is not clear why $ZnCl_2$ should not react with zeolite protons releasing HCl.

2. The reaction mechanism of propane aromatization over Zn/HZSM-5 is not fully unravelled. Guisnet et al. [1991] assume that the reaction occurs via a bifunctional mechanism; Zn catalyzes dehydrogenation of alkanes whereas the acidic sites oligomerize alkene. Our recent data on Ga/HZSM-5, however, shows that both functions cooperate even in the alkane activation step.

3. Because the catalytic reaction occurs in a reducing atmosphere, it is unavoidable that some of the Zn is reduced to the metal. The quantitative data on the reducibility of Zn in HZSM-5 is rather unknown.

Previously [Kwak and Sachtler, 1993], we prepared Ga/HZSM-5 catalysts by subliming $GaCl_3$ into the pores of the zeolite; the catalysts were characterized by H_2-TPR (temperature programmed reduction), CO-TPR, FTIR (Fourier-transform infrared), TPMS (temperature programmed mass spectrometry), and catalytic tests. As a logical extension, we now address the problem of incorporating Zn in HZSM-5 by the same chemical vapor phase deposition method using two precursors, i.e., $ZnCl_2$ and ZnO.

EXPERIMENTAL

1. Catalyst Preparation

The samples prepared by aqueous ion exchange method will be called Zn/HZSM-5(IE). A 250 ml solution of 0.01 M Zn-$(NO_3)_2$ hydrate (Aldrich Chemical, 99.99%) was added dropwise to an aqueous solution containing 7 g of HZSM-5 (from UOP, Si/Al=20.5) at a pH of 3.5. During ion exchange, the content was stirred vigorously for 48 h. After ion exchange, the slurry was filtered and washed with doubly distilled water followed by calcination at 500°C for 2 h. The final concen-

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tration of Zn is 0.88%.

Samples prepared by sublimation (CVD) of $ZnCl_2$ will be called ZnCl$_2$/HZSM-5(Su). Predetermined amounts of $ZnCl_2$ (Aldrich Chemical, 99.999%) were mixed with dried HZSM-5, transferred to reactors and sealed in a glove box. Two Ar flow rates were adopted for sublimation, viz., 40 ml/min and 180 ml/min. The reactors were heated from room temperature (RT) to 600°C at a rate of 0.5°C/min. At 600°C, the preparation was continued for 24 h. During sublimation, the effluent gas from the reactor was absorbed with a 0.1 M NaOH solution. These catalysts are analyzed to have 1.71% and 3.96% Zn respectively.

Catalysts prepared by subliming ZnO (Aldrich Chemical, 99.999%) following an analogous method to the above will be called ZnO/HZSM-5(Su). In this method, heating was applied from RT to 500°C at 0.5°C/min. The mixture was kept at 500°C for 2 h followed by heating to 600°C at a rate of 1.7°C/min. Finally the sample was heated for additional 48 h at 600°C. During preparation, the Ar flow rate was set at 40 ml/min. This sample contains 1.38% Zn.

2. Temperature Programmed Studies

To monitor the interaction between ZnO or $ZnCl_2$ with HZSM-5 and to analyze the released gas, a mass spectrometer system similar to the one described previously [Augustine et al., 1989] was used. Mixtures of ZnO and HZSM-5 or $ZnCl_2$ and HZSM-5 were used for the TPMS measurements. Predried HZSM-5 (500 mg) was mixed either with ZnO (50 mg) or $ZnCl_2$ (30 mg) in a glove bag and transferred to a reactor. The mixture was then sealed with Teflon valves and attached to a dedicated MS system. It was subjected to heating from −60 to 700°C (kept 1 h at 700°C) at 8°C/min under the Ar flow of 30 ml/min (standard ramp and flow rates for all TP studies).

TPR runs were done with ZnO and four Zn/HZSM-5 catalysts described above using a TCD cell as described elsewhere [Kwak and Sachtler, 1993].

The acid sites were characterized by NH$_3$-TPD. The samples were first saturated with anhydrous ammonia (99.99% min, Matheson) for 30 min at 120°C. After purging with He at the same temperature for 1 h, the samples were transferred to a TP system similar to the TPR apparatus. The TPD was run from 120 to 700°C (30 min at 700°C) in He.

The coke content of ZnO/HZSM-5(Su) was compared with that of HZSM-5 by temperature programmed oxidation with on-line mass spectrometry, TPOMS, using the same system as TPMS. After 4 h on stream at 530°C at a WHSV of 42 h^{-1} in propane, the catalytic test was terminated by purging with Ar for 15 min at 530°C. After cooling to RT, the same procedure as for TPMS was followed using 5% O$_2$ in He. The mass spectrometer was calibrated with pulses of CO$_2$.

3. Chlorine Contents

For ZnCl$_2$/HZSM-5(Su) catalysts, the chlorine contents were analyzed with a AgNO$_3$-HNO$_3$-isopropyl alcohol solution using an automatic Mettler DL 40RC titrator. The Cl content is 0.30 wt% for 1.71 ZnCl$_2$/HZSM-5(Su) and is 0.91 for 3.96 ZnCl$_2$/HZSM-5(Su).

4. Catalytic Tests

Propane conversion was carried out in a fixed-bed microreactor at 530°C as described previously [Kwak and Sachtl-

er, 1994].

RESULTS

1. Temperature Programmed Studies

TPMS spectra for ZnO (trace a), undried HZSM-5 (trace b), and a mixture of ZnO and predried HZSM-5 (trace c) are shown in Fig. 1. ZnO does not adsorb water evidenced by no mass 18 signal upon heating to 500°C. In contrast, undried HZSM-5 gives a huge peak between 100 and 300°C. For the physical mixture, there's no peak before 500°C. In this case, a new peak is found for temperature >530°C.

Fig. 2 shows TPMS spectra for a physical mixture of $ZnCl_2$ and predried HZSM-5. The signal of mass 36 (trace a) shows that the partial pressure of HCl is high even at low temperature. As the sample is heated, the intensity of signal drops slowly but strongly increases at 500°C. No water is released until 270°C (trace b). At 520°C, a second peak is observed.

TPR profiles for ZnO and four different Zn/HZSM-5 samples are shown in Fig. 3. Bulk ZnO is very difficult to reduce; it shows a peak with a maximum at 680°C (trace a). An intense peak with a T_{max} at 386°C reported by Yang et al. [1989] is not detectable. The degree of reduction expressed as the ratio of H$_2$
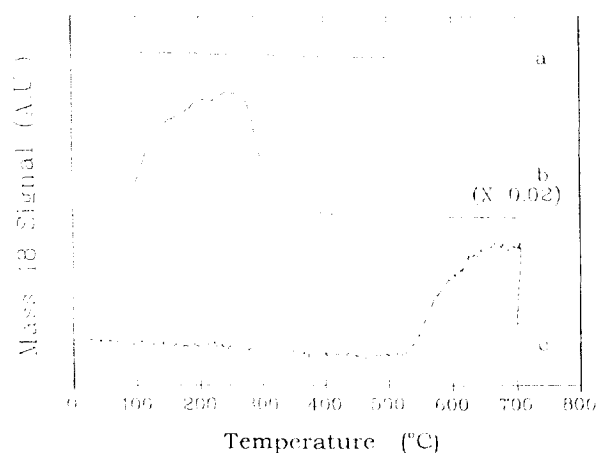

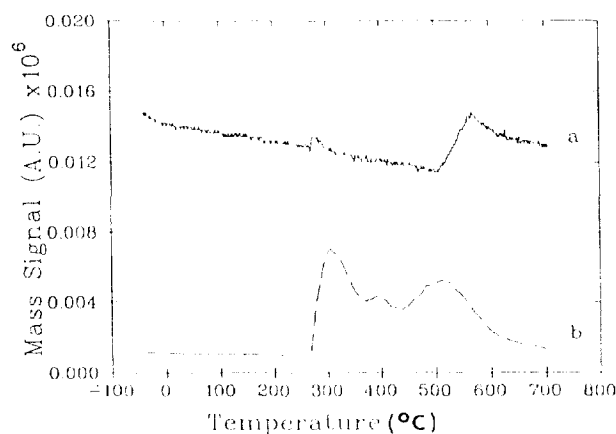Fig. 1. TPMS in He of (a) ZnO; (b) Undried HZSM-5; (c) ZnO + dried HZSM-5.

Fig. 2. TPMS of ZnCl$_2$ and HZSM-5 mixture: (a) m/e 36; (b) m/e 18.

consumption to Zn load, H_2/Zn, is very low for the oxide structure (0.005, Table 1). The ion exchanged sample shows a very poor TPR profile (trace b); the degree of reduction is low (0.19). In the case of ZnO/HZSM-5(Su), however, two peaks are found at 500 and 650°C (trace c). For this sample, the ratio of H_2/Zn is 0.56. For samples prepared with $ZnCl_2$, the TPR profiles are quite different from those of the ZnO/HZSM-5(Su) catalysts. For both samples, a T_{max} at 500°C is observed. For the 1.71% sample, a second broad peak starts after 570°C (trace d) whereas, for the 3.96% sample, a peak at 750°C is noticeable (trace e). The H_2/Zn ratio for these catalysts decreases with increasing loading.

For the temperature programmed desorption of NH_3 from HZSM-5 [Fig. 4(a)], two major peaks are found at 270°C (peak l) and 500°C (peak h). The positions of these peaks are shifted 55 (peak l) to 65°C (peak h) toward higher temperature compared with the published data [Yang et al., 1989]. As more Zn is added, the intensity of peak h decreases gradually while that of peak l is constant (Table 2). No visible shift in the T_{max} is obtained upon adding Zn. Unlike Ga/HZSM-5 catalysts [Kwak
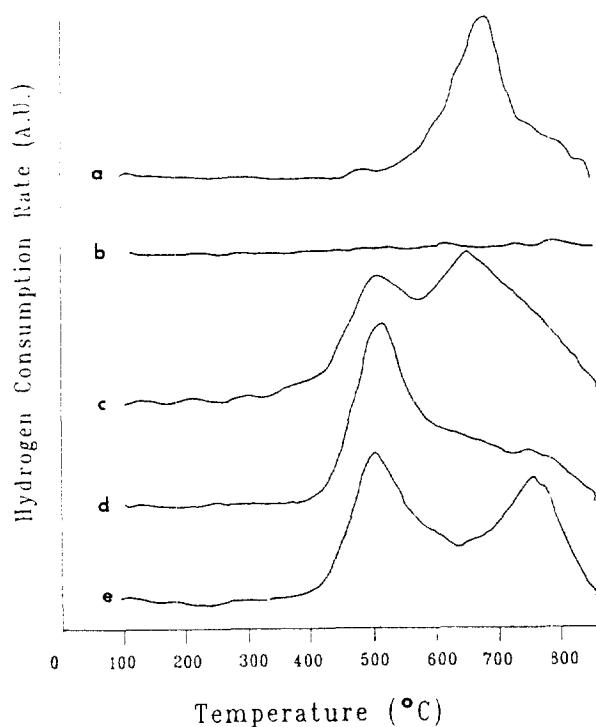
and Sachtler, 1994], no distinguishable peak from Lewis acid sites is found between these two principal peaks.

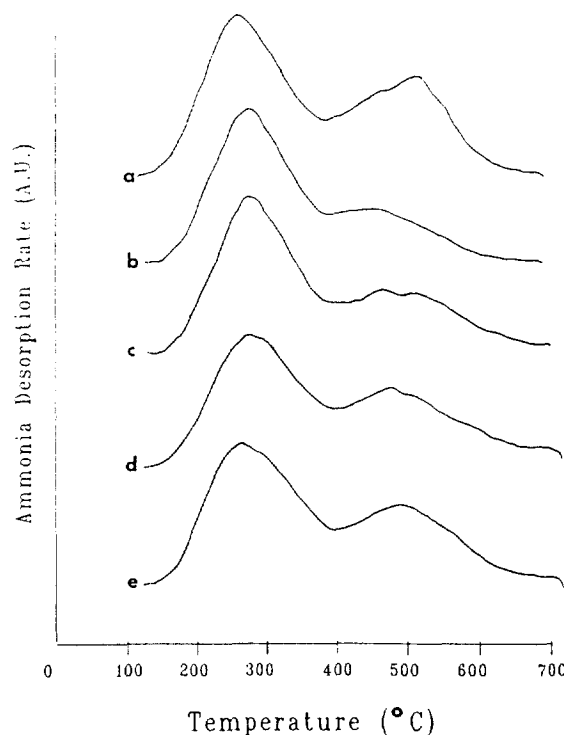Fig. 5 shows TPOMS spectra for HZSM-5 (trace a) and ZnO/

Fig. 4. NH₃-TPD spectra of (a) HZSM-5; (b) 3.96% ZnCl₂/HZSM-5(Su); (c) 1.71% ZnCl₂/HZSM-5(Su); (d) 1.38% ZnO/HZSM-5(Su); (e) 0.88% Zn/HZSM-5(IE).

Table 2. Summary of NH₃-TPD results over Zn catalysts

Sample	Uptake (NH₃/H⁺)	T_{max} l	T_{max} h	Uptake of P_l	Uptake of P_h
HZSM-5	1.68	265	500	0.87	0.81
0.88% Zn/HZSM-5(IE)	1.52	265	500	0.86	0.66
1.38% ZnO/HZSM-5(Su)	1.39	270	490	0.81	0.58
1.71% ZnCl₂/HZSM-5(Su)	1.39	270	470	0.94	0.45
3.96% ZnCl₂/HZSM-5(Su)	1.10	270	460	0.93	0.17

Fig. 3. TPR profiles of (a) ZnO; (b) 0.88% Zn/HZSM-5(IE); (c) 1.38% ZnO/HZSM-5(Su); (d) 1.71% ZnCl₂/HZSM-5(Su); (e) 3.96% ZnCl₂/HZSM-5(Su).

Table 1. Summary of TPR results over Zn catalysts

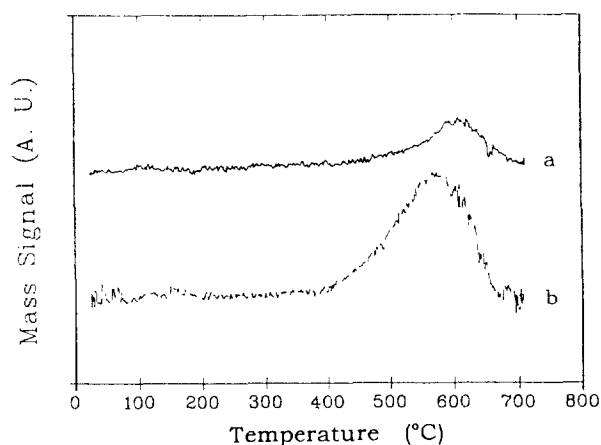| Sample	H₂/Zn ratio	T_{max} 1	T_{max} 2	T_{max} 3	% Area 1	% Area 2	% Area 3
ZnO	4.7E-3		670			>95	
0.88% Zn/HZSM-5(IE)	0.19	*			32	68	
1.38% ZnO/HZSM-5(Su)	0.56	500	660	-	31	69	
1.71% ZnCl₂/HZSM-5(Su)	0.35	507	640	740	43	15	42
3.96% ZnCl₂/HZSM-5(Su)	0.14	500	645	750	37	13	50

*Peak too broad or too noisy.

Fig. 5. TPOMS profiles of (a) HZSM-5; (b) 1.38% ZnO/HZSM-5(Su).

HZSM-5(Su) (trace b). In both cases, only one peak is observed. The oxidation of carbonaceous deposits on HZSM-5 gives a CO_2 peak with a maximum at 610°C. From ZnO/HZSM-5(Su), a peak with T_{max} at 570°C is detected. Variation in O_2, CO, CO_2, and H_2O partial pressure is given in Fig. 6 for ZnO/HZSM-5 as an example. Integration of the peak area gives a coke content of 0.92% for HZSM-5 and 2.19% for ZnO/HZSM-5(Su) respectively.

2. Propane Conversion

Fig. 7 shows the effect of pretreatment conditions on the conversion for 3.96% $ZnCl_2$/HZSM-5(Su). When the sample is prereduced, the activity changes very little with time-on-stream. The activity is lower after reduction at higher temperature. For a reduction temperature (T_r)=580°C, the activity is 11% lower than that of T_r=530°C. This is due to the elution of Zn^0 generated by the reduction of Zn ions or ZnO [Chu and Chester, 1983] suggesting that a partially reduced form of Zn is active. When the catalysts are preoxidized, the activity develops with

time on stream up to 250 min, regardless of the space velocity. After this induction period, the activity drops. The same is true even for the sample prereduced at 530°C.

The product molar selectivity over the ZnO/HZSM-5(Su) sample is plotted vs. conversion in Fig. 8. At very low conversion (~0), only methane, ethene, and propene are obtained. Almost equal amounts of methane and ethene are formed in accordance with the cracking mechanism of pentacoordinated carbonium ions [Kwak et al., 1994]. As the conversion increases, the selectivities to ethene and butenes pass through maxima accompanied by an increase in selectivity to aromatics. Selectivities to methane and ethane increase with the conversion as a result of secondary transformation of reaction intermediates.

For 3.96% $ZnCl_2$/HZSM-5(Su), the selectivity vs. conversion plot is shown in Fig. 9. Unlike ZnO/HZSM-5(Su) sample, only

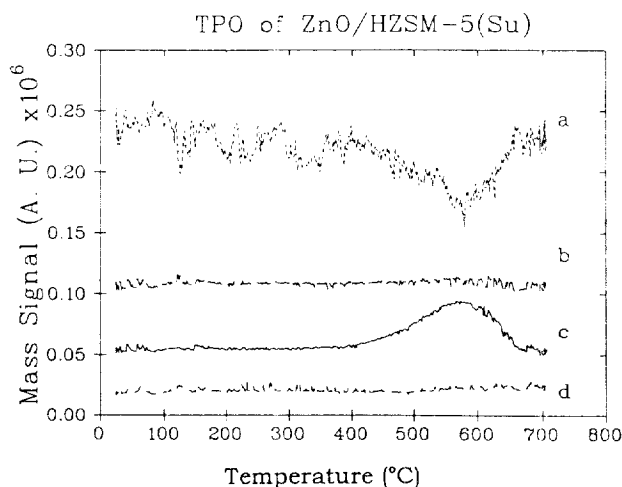

Fig. 6. TPOMS spectra of 1.38% ZnO/HZSM-5(Su): (a) m/e 32; (b) m/e 28; (c) m/e 44; (d) m/e 18.
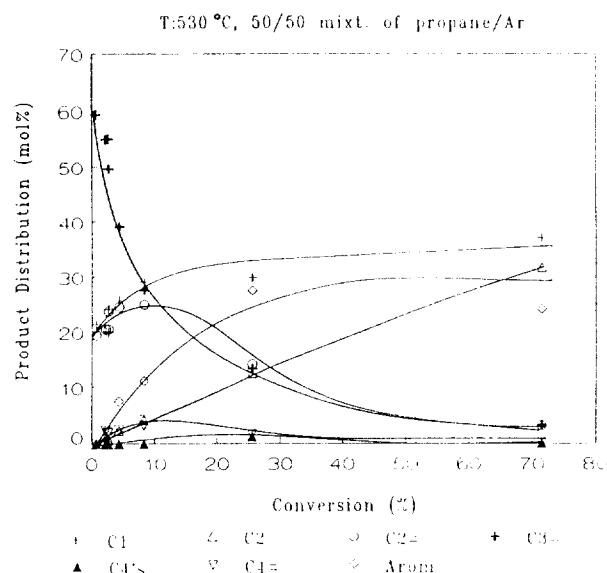

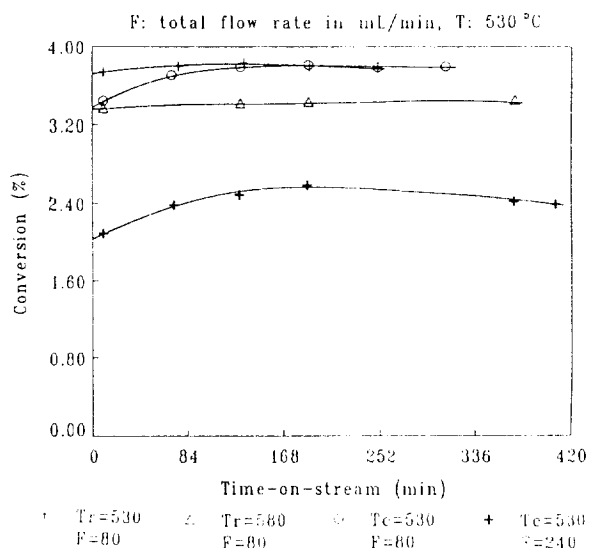Fig. 8. Effect of conversion on product distribution over 1.38% ZnO/HZSM-5(Su).

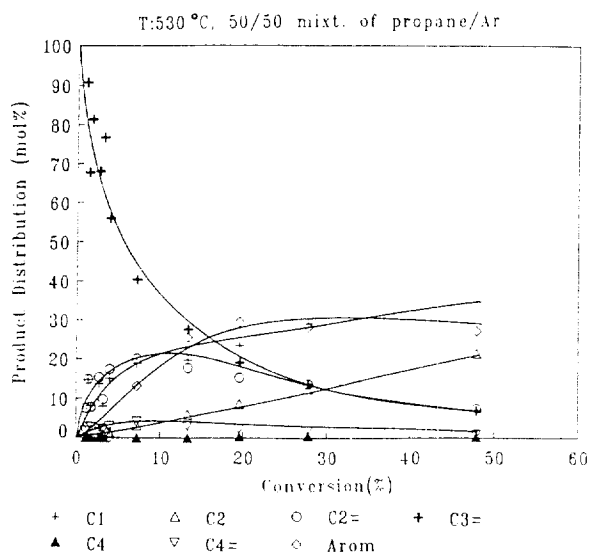Fig. 7. Effect of pretreatment on the activity over 3.96% $ZnCl_2$/HZSM-5(Su).

Fig. 9. Effect of conversion on product distribution over 3.96% $ZnCl_2$/HZSM-5(Su).

Table 3. Propane conversion at 530°C and WHSV of 42 h⁻¹ on Zn/HZSM-5

	HZSM-5	0.88% Zn	1.38% Zn	1.77% Zn	3.96% Zn
Selectivity methane	26.92	30.10	29.91	24.52	19.75
Ethane	4.68	5.18	12.51	6.06	6.02
Ethene	38.56	20.62	14.13	17.84	17.72
Propene	26.79	17.16	13.31	20.31	27.65
Butanes*	2.35	-0.37	1.28	0.05	-0.01
Butenes	0.69	2.14	1.70	2.94	3.11
Aromatics	0	24.93	27.54	28.49	25.54
Conversion	7.25	15.21	25.59	16.89	13.36
H/C ratio	2.60	2.42	2.49	2.30	2.22

*Butane is in the feed.
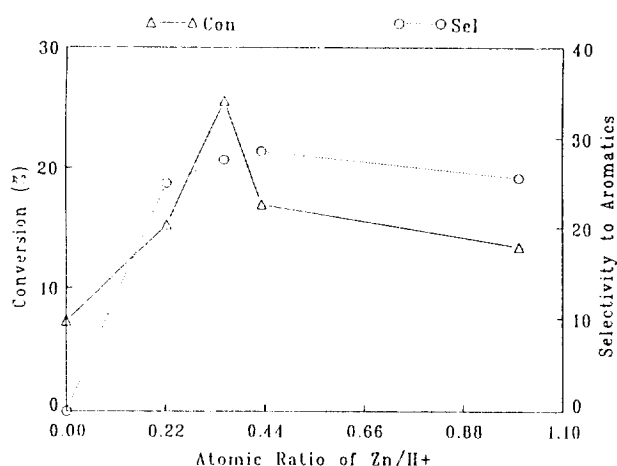
Fig. 10. Effect of Zn/proton ratio on propane conversion and selectivity to aromatics.

propene is obtained at low conversion. This is believed to result from the reduced acidity of the catalysts due to the high degree of ion exchange of protons by Zn. In this case, the overall trend is almost the same as ZnO/HZSM-5(Su) sample.

Catalytic activity and selectivity to aromatics for propane conversion at a space velocity (WHSV) of 42(/hr) are compared in Table 3 and Fig. 10. All the Zn-containing catalysts exhibit better catalytic performances than that of HZSM-5. Among four Zn/HZSM-5 samples, the activity is highest on ZnO/HZSM-5(Su). It is interesting that the activity drops suddenly at a Zn/proton ratio of 0.35 while the selectivity to aromatics is almost the same. Selectivity to methane decreases as the Zn concentration in the catalysts goes up indicating that the activity of acid-catalyzed cracking is diminished. The material balance also shows that as the Zn content increases, the H/C ratio decreases suggesting an increase in dehydrogenating activity.

DISCUSSION

1. Incorporation of Zn and the Nature of Zn Species

When ZnO reacts with protons:

$$ZnO + 2H^+ = Zn^{2+} + H_2O \tag{1}$$

Zn^{2+} ions are formed with water. As shown in Fig. 1, water is formed from a physical mixture of ZnO and dried HZSM-5 at elevated temperature (>500°C) confirming the occurrence of the ion exchange reaction (1). The consumption of protons is also evidenced by the decrease in the peak area of the peak h which is known to be the desorption of NH_3 from ion-exchangeable Brønsted acid sites (Table 2) [Kwak and Sachtler, 1994; Yang et al., 1989]. It is known that in the absence of acid sites, Ga_2O_3 is very difficult to reduce [Kwak and Sachtler, 1993; Price and Kanazirev, 1990]. It is also known that a TPR peak from zeolite-encaged Ga ions comes at higher temperature than that from finely dispersed Ga oxide particles [Kwak and Sachtler, 1993]. In analogy, from TPR spectra, a peak with a maximum at 650°C is attributed to the reduction of Zn^{2+} and the peak with T_{max} at 500°C to that of ZnO particles in the presence of protons [Fig. 3(c)]. All these data consistently support the occurrence of the exchange reaction (1).

If $ZnCl_2$ were used as a precursor instead of ZnO, one would expect:

$$ZnCl_2 + H^+ = (ZnCl)^+ + HCl \tag{2a}$$

$$(ZnCl)^+ + H^+ = Zn^{2+} + HCl \tag{2b}$$

HCl evolution from the mixture. The presence of the $(ZnCl)^+$ ion in the aqueous system is reported; its free energy of formation is -65.8 (kcal/mole) [Aylett, 1975]. The formation of HCl is monitored by the mass spectrometer [Fig. 2(a)]. At the same time, much water is also detected [Fig. 2(b)]. Its only source is $ZnCl_2$ since HZSM-5 has been predried. Because $ZnCl_2$ is hygroscopic, the presence of some moisture is unavoidable. In the presence of water:

$$ZnCl_2 + 2H_2O = Zn(OH)_2 + 2HCl \tag{3a}$$

$$Zn(OH)_2 = ZnO + H_2O \tag{3b}$$

ZnO is formed since zinc hydroxide is easily decomposed into ZnO for temperature >125°C [Farnsworth and Kline, 1968]. The presence of ZnO is manifest from the TPR spectra [Fig. 3(d) and (e)]. The high partial pressure of HCl even at low temperature suggests that reaction (3a) occurs to some extent [Fig. 2(a)]. Water adsorbed by $ZnCl_2$ begins to be released at 300°C [Fig. 2(b)]. Another water peak with a T_{max} at 520°C is believed to originate from the reaction between protons and ZnO formed by reactions [(3a)-(3b)]. Therefore, we can assume three kinds of species from the mixture of $ZnCl_2$ and HZSM-5, viz., ZnO, Zn^{2+} and probably $(ZnCl)^+$ ions. From Fig. 3(d), a small peak at a T_{max} of ca. 650°C due to the reduction of Zn^{2+} is observed. As more Zn is added, a new peak at 750°C emerges. This peak is not seen for ZnO/HZSM-5(Su). From the NH_3-TPD of the 3.96% sample, we can observe a substantial decrease in the concentration of the Brønsted acid sites (Table 2). If the only ionic species in the catalysts is Zn^{2+}, this decrease in the acid sites should be reflected by a single TPR peak with a T_{max} of 650°C. Consequently, it is clear that the peak with a maximum at 750°C (peak 3) does not come from the reduction of Zn^{2+} but is, anyway, related to ionic Zn. It was proposed by Guisnet et al. [1991] that $ZnCl_2$ may react with zeolitic protons [reaction (2a)] based on the Cl/Zn atomic ratio of 1 from their

Zn/HZSM-5 sample prepared by subliming $ZnCl_2$ into HZSM-5 although they denied the possibility of the proton exchange by Zn. From $AgNO_3$ titration, we also confirmed the presence of Cl^- ion on these catalysts. Combining the titration and the TPR data (Table 1, area of peak 3), the avearge ratio of Cl/Zn of 0.81 is obtained for the peak 3 from both samples. Therefore, it is temporarily concluded that the peak at 750°C results from the reduction of $(ZnCl)^+$ despite the Cl/Zn ratio is not exactly one. The difficulty of the deconvolution of the TPR spectra might have caused this error. It is noteworthy that the $(ZnCl)^-$ species in $ZnCl_2$/HZSM-5(Su) samples is so stable that even the oxidation with O_2 at 500°C for 2 h does not affect the TPR profile.

The interaction of $ZnCl_2$ with zeolitic protons seems to be weaker than that of $GaCl_3$ since the majority of the chloride is observed to be eluted without any reaction at a higher carrier flow rate. This is in marked contrast with the observations with $GaCl_3$. This might be a cause of a failure by Guisnet et al. [1991] to detect a change in acidity.

2. Acidity

In the previous work [Kwak and Sachtler, 1994], it was shown that the peak 1 represents the desorption of physisorbed NH_3 [Haag, 1992] and NH_3 adsorbed on non-exchangeable acidic sites and the peak h is responsible for that of chemisorbed NH_3 from exchangeable Brønsted acid sites. In the case of Ga/HZSM-5, as the Brønsted acid sites are exchanged by Ga, Lewis acid sites appear only for high Ga loading. For Zn-exchanged catalysts, it is evident that Brønsted acid sites are substituted by Zn with any method used here (Table 2). However, remarkably, no Lewis acid sites are detected even at high Zn loading. Yang et al. [1989] also couldn't detect the appearance of Lewis acid sites by their NH_3-TPD for 2.0% Zn/HZSM-5 prepared by subliming ZnO. Instead, they detected an infrared (IR) band at 1455 cm^{-1} (Lewis acid band) by adsorbing pyridine. This was also confirmed by Kazansky et al. [1989] in IR studies. Therefore, we assume that the Lewis acid sites are not detected in ZnO/HZSM-5(Su) by TPD because of the rather low loading not because of the absence of the Lewis acid sites. If the existence of the Lewis acid sites depends on the loading, it should be visible on 3.96% $ZnCl_2$/HZSM-5(Su) sample. The absence of this peak from the TPD suggests that the major ionic species present in this catalysts do not adsorb large amounts of basic ligands. This suggests a weakly acidic or non-acidic nature of $(ZnCl)^-$.

In propane conversion, the selectivity to methane decreases with Zn loading. As methane formation is more likely due to decomposition of carbonium ions:

$$CH_3CH_2CH_3 + H^+ = CH_3C^-H_3CH_3 = CH_4 + C_2H_4 + H^+ \quad (4)$$
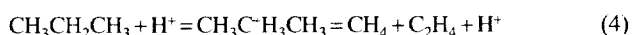
it follows that incorporation of Zn lowers the concentration of protons; for 3.96% $ZnCl_2$/HZSM-5(Su) sample, the initial selectivity to methane is zero. Thus, we conclude that Zn replaces zeolitic protons by ion exchange irrespective of preparation method.

3. Reaction Mechanism and Possible Role of Zn

We assume that HZSM-5 transforms propane into methane, ethene, and propene via cracking of a pentacoordinated car-

bonium ion [Haag and Dessau, 1984; Kazansky et al., 1989]. Besides the reaction (4) considered in the previous paragraphs, we have:

$$CH_3CH_2CH_3 + H^+ = CH_3C^+H_3CH_3 = C_3H_6 + H_2 + H^+ \quad (5)$$
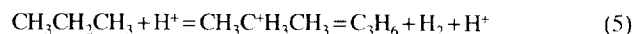
Hence, equal amounts of methane and ethene or of H_2 and propene are formed. When a dehydrogenating metal is added to HZSM-5, propene is formed also by dehydrogenation:

$$CH_3CH_2CH_3 = CH_2CHCH_3 + H_2 \quad (6)$$
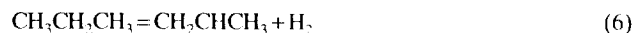
When extrapolating to zero conversion, equal amounts of methane and ethene (selectivity=20.5) are indeed formed over ZnO/HZSM-5(Su). This supports the validity of the carbonium ion mechanism (Fig. 8). Previously [Kwak et al., 1994], it was estimated that, for propane activation on HZSM-5, the contribution of acid-catalyzed cracking (4) is 63% and that of acid-catalyzed dehydrogenation (5) is 37%. If this result is extended to ZnO/HZSM-5(Su) for propene formation, 21% of propene is formed via cracking path [reaction (5)] and 79% by metal-catalyzed dehydrogenation [reaction (6)]. The addition of a small amount of Zn thus changes the reaction mechanism from acid cracking to a combination of acid cracking and dehydrogenation. This conclusion is at variance with the statement of Guisnet et al. [1991] that the formation of propene via a carbonium ion intermediate is negligible.

On 3.96% $ZnCl_2$/HZSM-5(Su), however, no cracked products are formed at zero conversion in accordance with the results of Guisnet et al. [1991] (Fig. 9). This does not imply that there are no acid sites; these are necessary for the formation of aromatic hydrocarbons via oligomerization of olefins. It is rather proposed that propane is mainly activated by the dehydrogenation sites, which might also be better accessible at high Zn loading when many acid sites have been replaced by ion exchange [Kazansky et al., 1989]. This kind of steric hindrance was indicated by N_2 adsorption [Guisnet et al., 1991]. It is not clear whether the difference in the propane activation mechanism for different catalysts comes from the difference in the Zn loading or from the different nature of the Zn species. However, as shown by the selectivity to methane (Table 3), the reaction mechanism seems to be mainly affected by the loading.

The introduction of Zn to HZSM-5 enhances not only propane conversion but also selectivity to aromatics (Fig. 8, 9, and Table 3). If the formation of aromatics were catalyzed by hydrogen transfer on acidic sites, this selectivity should decrease with increasing Zn content. In reality, however, the selectivity increases with metal loading and stays at a high value. This strongly suggests that Zn effectively dehydrogenates intermediates into aromatics [Guisnet et al., 1991; Arroyo et al., 1991] contrary to the suggestion by Bursian et al. [1991] (Table 3). The decrease of the H/C ratio with Zn loading also supports the hypothesis that dehydrogenation is catalyzed by Zn.

Little is known about the precise nature of Zn species that catalyzes the propane conversion. Our data suggest that a slightly reduced form of Zn, Zn^{x+} with x<2, is active in the aromatization (Fig. 7). It is conceivable that the induction period reflects the time required for forming Zn^{x+}, as the catalysts prereduced at 530°C are somewhat more active than the preox-

idized catalysts. The decrease in the activity after 4 or 5 h is probably due to the carbonaceous deposits [Fig. 5(b)] on this catalysts rather than to metal loss, since the degree of reduction at this temperature is very low (Table 1). The Zn^{r+} species, acting as a Lewis acid site, may cleave C-H bonds by pulling a H^- ion from the molecule and forming $(Zn-H)^{r-1}$. This is in agreement with a published IR evidence [Kazansky et al., 1989]. Thus, on Zn/HZSM-5, more hydrogen-deficient coke is formed than on HZSM-5. The low intensity of this Lewis acid sites from the 1.71% $ZnCl_2$/HZSM-5(Su) catalysts may be responsible for a sudden drop in activity of these catalysts (Fig. 10). Further decrease in activity and selectivity to aromatics for 3.96% $ZnCl_2$/HZSM-5(Su), however, indicates that both acidic and metallic sites are necessary to maintain good catalytic activity. Therefore, we believe there's an optimum ratio of Zn/H^+ in the vicinity of 0.3. At this Zn concentration, the synergism between Zn and Brφnsted acid sites is expected to occur like Ga/HZSM-5 [Buckles et al., 1991; Kwak and Sachtler, 1994].

CONCLUSIONS

The following conclusions can be drawn from the experimental data presented in this paper:

1. Exchange of protons with Zn ions takes place with all preparation methods, ion exchange (IE) or CVD (Su), irrespective of the type of catalytic precursor, ZnO or $ZnCl_2$.

2. The reducibility of Zn in HZSM-5 depends on the method of precursor introduction and the type of precursor.

3. Catalysts prepared by CVD of ZnO into HZSM-5, ZnO/HZSM-5(Su) contain ZnO particles and Zn^{2+} ions. They show relatively high reducibility and good catalytic performance.

4. Catalysts prepared by CVD of $ZnCl_2$ into HZSM-5, $ZnCl_2$/HZSM-5(Su), form ZnO, Zn^{2+}, and other ions, probably $(ZnCl)^+$. They show poor reducibility and low activity.

5. Unlike catalysts prepared by CVD of $GaCl_3$ into HZSM-5, no Lewis acid sites are detected by NH_3-TPD of $ZnCl_2$/HZSM-5(Su). The low density of Lewis acid sites might be one cause for the lower activity of these catalysts.

6. On 1.38% ZnO/HZSM-5(Su), propane is activated by metal-catalyzed dehydrogenation and acid-catalyzed cracking of pentacoordinated carbonium ions. Zn enhances the dehydrogenating activity and the selectivity to aromatics. On 3.96% $ZnCl_2$/HZSM-5(Su), propane is solely activated by dehydrogenation. This difference in propane activation mechanism seems to be more affected by Zn loading than the nature of the Zn species in the zeolites.

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