

# Conversion of Methane to Benzene over Transition Metal Ion ZSM-5 Zeolites

## I. Catalytic Characterization

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The conversion of methane to benzene in the absence of oxygen has been investigated over different TMI/H-ZSM-5 zeolites (with TMI = Mo, Fe, V, W, and Cr) as a function of the preparation and treatment method, the metal ion loading, and the zeolite acidity. Nonoxidative methane activation is characterized by an induction period prior to the formation of benzene, toluene, and naphthalene. During this induction period the supported metal oxide is reduced and CO, CO<sub>2</sub>, and H<sub>2</sub>O are formed. Optimum catalytic performance was obtained for CO-prereduced 2–4 wt% TMI/H-ZSM-5 zeolites, and their activities decreased in the order: Mo (18.3) > W (10.8) > Fe (5.7) > V (3.9) > Cr (1.5). The numbers in parentheses are the rates of methane reaction (molec. reacted/metal atom/h) obtained after 3 h on-stream. Impregnated materials always had a higher activity and shorter initial induction period than solid state ion-exchanged materials, and the induction period decreased with increasing time at moderate reduction temperature and with increasing metal oxide loading. Based on a detailed comparison of the different systems, it is evident that the catalytic properties depend on the presence of Brønsted acid sites and the distribution of the TMI's in the zeolite material. © 1998 Academic Press

## INTRODUCTION

The catalytic conversion of methane to desired commodity chemicals is a challenging approach for the utilization of natural gas resources (1, 2). Several recent studies have demonstrated that methane can be converted to benzene in the absence of an oxidant, such as oxygen, and the main literature results are summarized in Table 1 (3–15). It is clear that different transition metal ions (TMI's), such as Mo, Cu, Zn, and Cr, are able to activate methane and that Mo/H-ZSM-5 is the most promising catalytic system. However, some active TMI's, in particular Mo, show little or no activity in other characterization studies (3, 4). Thus, it seems

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that preparation and treatment conditions play a crucial role in the activation of these materials. Furthermore, the exact dehydroaromatization mechanism, the distribution of TMI's in the zeolite material, and the phase responsible for methane activation are still a matter of debate.

To resolve these issues, we have performed a systematic study on the effect of TMI, as well as the catalyst preparation and treatment, on the activation of methane. Mo, Fe, Cr, W, and V/H-ZSM-5 materials, prepared by either impregnation and solid state ion exchange, were compared. Solid state ion exchange of zeolites with volatile metal chlorides is a convenient method to introduce metal ions at exchange sites (16, 17). Therefore, special emphasis was placed on the distribution of TMI's, the role of the induction time and the active phase. In this paper, a detailed discussion of the catalytic performances of these materials will be given. Part II of this study will focus on the identification of the active phases for methane activation by X-ray photoelectron spectroscopy (18).

## EXPERIMENTAL

### 1. Catalyst Preparation

Different TMI/H-ZSM-5 catalysts were prepared starting from commercial H-ZSM-5 (PQ Corp., CBU 5020E) having a Si/Al ratio of 25. Fully exchanged H-ZSM-5 was obtained by ion exchange of 10 g of the zeolite with a 300 ml of 1 M aqueous solution of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>, EM Science) at 80°C for 12 h, followed by drying at 90°C overnight and calcination at 500°C for 5 h. Partially exchanged H, Na-ZSM-5 materials were prepared in a similar way using aqueous mixtures of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>, EM Science) and sodium chloride (NaCl, EM Science) in ratios of 5:1, 3:1, and 2:1. In addition, a fully exchanged Na-ZSM-5 sample was prepared using a 1 M sodium chloride (NaCl, EM Science) solution.

The resulting zeolite materials were then further used for impregnation or solid state ion exchange with an

TABLE 1

## Literature Survey of Nonoxidative Dehydrogenation over Transition Metal Ion-Loaded ZSM-5 Zeolites

Catalytic system	Active phase	Mechanism for catalytic activation of methane	Distribution of transition metal ions	References
Ru, X/H-ZSM-5 or Pt, X/H-ZSM-5 with X = Ga, Zn, or Cr	Metal/metal oxide	$\text{MO} + \text{CH}_4 \rightarrow \text{M-OH} + \text{CH}_3^*$ $2\text{CH}_3^* \rightarrow \text{C}_2\text{H}_6$	Not discussed	(3, 4)
Mo/H-ZSM-5	$\text{MoO}_3$	$\text{CH}_4 + \text{MoO}_3 \rightarrow \text{CH}_3\text{-H} + \text{MoO}_3$ $\rightarrow \text{H}^- - \text{CH}_3^+ + \text{MoO}_3$ $\rightarrow \text{Mo}=\text{CH}_2$	$\text{MoO}_3$ crystallites and octahedral agglomerates ( $\text{NH}_4\text{OH}$ extractable) $\text{MoO}_4^{2-}/\text{Al}_2(\text{MoO}_4)_3$ ( $\text{NH}_4\text{OH}$ non-extractable)	(5, 7)
Cu/H-ZSM-5	CuO	Carbenium ion mechanism	Not discussed	
Zn/H-ZSM-5	ZnO	$\text{CH}_4 + \text{Zn}^{2+}(\text{s}) \rightarrow \text{CH}^+(\text{s}) + [\text{Zn-H}]^+$	Not discussed	
Mo/H-ZSM-5	$\text{MoO}_x$	$\text{CH}_4 \rightarrow \text{CH}_3^* + \text{H}^*$ $2\text{CH}_3^* \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	Active phase in the zeolite channels	(8, 9)
Mo/H-ZSM-5	$\text{Mo}_2\text{C}/\text{Mo}_x\text{-C-MoO}_x$	$\text{CH}_4 + \text{O}(\text{s}) \rightarrow \text{CH}_3^* + \text{OH}(\text{s})$ $2\text{OH}(\text{s}) \rightarrow \text{H}_2\text{O} + \text{O}(\text{s})$ $2\text{CH}_3^* \rightarrow \text{C}_2\text{H}_6$	Not discussed	(10–12)
Mo/H-ZSM-5	$\text{Mo}_2\text{C}$	$\text{C}_2\text{H}_4$ formed on $\text{Mo}_2\text{C}$ and converted to aromatics at acid centers	Active phase is predominantly at outer surface	
Fe/H-ZSM-5	$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	$\text{C}_2\text{H}_4$ formed on transition metal ions and converted to aromatics at acid centers	Active phase is predominantly at outer surface	(15)

appropriate TMI salt. For impregnation, aqueous solutions of ammonium paramolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , Spectrum), iron (III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Aldrich), ammonium vanadate ( $\text{NH}_4\text{VO}_3$ , Fisher), ammonium paratungstate ( $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6$ , Fluka) and chromium (VI) trioxide ( $\text{CrO}_3$ , Spectrum) were used. Molybdenum (III) chloride ( $\text{MoCl}_3$ , Aldrich), iron (III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Spectrum), vanadium (III) chloride ( $\text{VCl}_3$ , Aldrich), tungsten (IV) chloride ( $\text{WCl}_4$ , Aldrich), and chromium (III) chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , Spectrum) were used for the solid state ion exchange reaction. Impregnated samples were prepared according to the incipient wetness method, followed by drying at  $90^\circ\text{C}$  overnight and calcination at  $500^\circ\text{C}$  for 5 h. Solid state ion-exchanged materials were prepared by physically mixing the appropriate amounts of zeolite powder and TMI-salt in a mortar, followed by drying at  $90^\circ\text{C}$  overnight and calcination at  $500^\circ\text{C}$  for 5 h. Clearfield and Troup (19) have demonstrated that solid–solid reactions between the hydrogen form of an ion exchange material and a transition metal chloride afford an alternative method for incorporating transition metal ions into the ion exchanger. The driving force for this reaction is the formation of gaseous HCl. The reaction of  $\text{MoOCl}_4$  with a H–Y zeolite was found to be essentially quantitative, as determined from the amount of HCl that evolved from the zeolite (20). The freshly prepared TMI/H-ZSM-5 samples were then crushed and sieved to 20/45 mesh sizes.

## 2. Catalyst Pretreatment and Characterization

Reactions were carried out in a flow system, using reactors constructed from alumina tubes (Coors, AD-998, 99.8%  $\text{Al}_2\text{O}_3$ ) having an internal diameter of 6.4 mm and containing 1.0 g of the catalyst. To minimize the contribution from any gas phase reactions, quartz chips filled the space above and below the catalyst beds in the flow reactors. A thermocouple in a smaller alumina tube was attached to the outside wall of each of the reactors. Reactant gases, which included 10%  $\text{N}_2/\text{CH}_4$  (UHP),  $\text{O}_2$  (UHP), He (UHP), and CO (UHP), were obtained from Matheson. The CO was purified to remove iron carbonyls by passing the CO stream at  $300^\circ\text{C}$  through an alumina tube, filled with quartz chips. The other gases were used without further purification. Gas flows were regulated by mass flow controllers (MKS Model 1159A). In the flow system, the catalyst was heated in an  $\text{O}_2$  flow at  $500^\circ\text{C}$  for 1 h, and flushed in He for 30 min (flow rate of 50 ml/min). Some catalysts were then reduced in a stream of CO for several hours at high temperatures (flow rate of 50 ml/min). After calcination and eventually reduction, the catalyst was subjected to a  $\text{CH}_4$  stream at  $750^\circ\text{C}$ . The GHSV was normally kept at  $800 \text{ h}^{-1}$ , although some experiments were conducted at lower and higher GHSV's.  $\text{N}_2$  in  $\text{CH}_4$  was used as an internal standard so that the  $\text{CH}_4$  conversion could be determined accurately and the coke formation during the reaction could be

evaluated from a carbon mass balance. Reaction mixtures were analyzed using a HP5890A gas chromatograph, equipped with a 5% Bentone 34 on Chromosorb W-AW column and a HayeSep D column. All studies were carried out at atmospheric pressure.

FT-IR spectra of the catalysts were obtained using a Perkin Elmer 2000 FT-IR spectrometer. Self-supported wafers of 10–15 mg/cm<sup>2</sup> were obtained by pressing the powdered catalysts. Each wafer was mounted on a fused-quartz bracket that was placed in an IR cell. The cell was equipped with KBr windows and a heated region into which the wafer could be raised and pretreated under vacuum at 500°C for 2 h. Spectra were recorded at room temperature after this pretreatment. The resolution was 4 cm<sup>-1</sup>, and corrections for variations in sample wafer thickness were made for all the spectra.

## RESULTS AND DISCUSSION

A survey of the catalytic performances of 2.0 wt% transition metal ion-loaded ZSM-5 zeolites for the reaction of methane at 750°C, in the absence of oxygen, is given in Table 2. This table summarizes the maximum methane conversion, and the maximum selectivity toward benzene, naphthalene, and aliphatic hydrocarbons (mainly C<sub>2</sub>–C<sub>3</sub>

hydrocarbons) as a function of the transition metal ion (Mo, Fe, V, W, and Cr), the preparation method (impregnation versus solid state ion exchange), and the pretreatment method (with or without CO prereduction at 500°C). A detailed discussion of this table will be given in the next three sections. Two other sections are devoted to the influence of the zeolite acidity and the metal loading on the methane activation process.

### 1. Effect of Transition Metal Ion

The results of Table 2 clearly show that the catalytic activity is strongly dependent on the identity of the transition metal ion and the pretreatment of the material. Optimum catalytic performance was obtained for TMI/H-ZSM-5 zeolites prereduced with CO. The activities decreased in the order: Mo > W > Fe > Cr. The value of 18.3 molec. CH<sub>4</sub> reacted/metal atom/h compares favorably with the value of 17 molec. CH<sub>4</sub> reacted/metal atom/h reported previously (14).

As an example, we will discuss the catalytic performances of V/H-ZSM-5 catalysts in more detail. The activities and product selectivities for the reaction of methane at 750°C and a space velocity of 800 h<sup>-1</sup> over a 2 wt% V/H-ZSM-5 catalyst are given in Fig. 1. The catalyst was prepared by impregnation and prereduction with CO at 500°C. Following an initial activation period during the first 2 h of reaction,

TABLE 2

Survey of the Catalytic Performances of 2.0 wt% Transition Metal Ion-Loaded ZSM-5 Zeolites in the Methane Reaction at 750°C

Transition metal ion	Preparation method <sup>a</sup>	CO <sup>b</sup>	Methane reaction		Maximum selectivity (%)		
			Conversion (%) <sup>c</sup>	Rate <sup>d</sup>	Benzene	Naphthalene	Aliphatic hydrocarbons
Mo	SOL	No	2.6	6.0	71.5	0	31.7
		Yes	7.5	17.4	71.2	5.9	32.6
	IMP	No	7.6	17.7	78.4	8.6	13.1
		Yes	7.9	18.3	72.2	13.6	12.8
Fe	SOL	No	0.8	1.2	0	0	17.7
		Yes	3.9	5.4	45.5	0	31.7
	IMP	No	4.1	5.7	61.8	3.7	19.4
		Yes	4.1	5.7	73.4	16.1	22.1
V	SOL	No	0.6	0.6	35.4	0	20.1
		Yes	0.6	0.6	35.5	0	19.1
	IMP	No	0.6	0.6	63.1	0	19.8
		Yes	3.2	3.9	31.6	6.3	20.4
Cr	SOL	No	0.2	0.3	0	0	20.1
		Yes	0.5	0.6	28.2	0	64.9
	IMP	No	0.3	0.3	19.4	0	58.6
		Yes	1.1	1.5	72.0	3.7	26.7
W	SOL	No	0.3	1.5	0	0	12.7
		Yes	2.3	10.2	40.6	0	18.5
	IMP	No	0.7	3.0	0	0	16.9
		Yes	2.4	10.8	50.8	0	20.1

<sup>a</sup> SOL, prepared via solid state ion-exchange; IMP, prepared via impregnation.

<sup>b</sup> 500°C for 6 h.

<sup>c</sup> After 3 h of reaction.

<sup>d</sup> Molecules CH<sub>4</sub> reacted/metal atom/h.

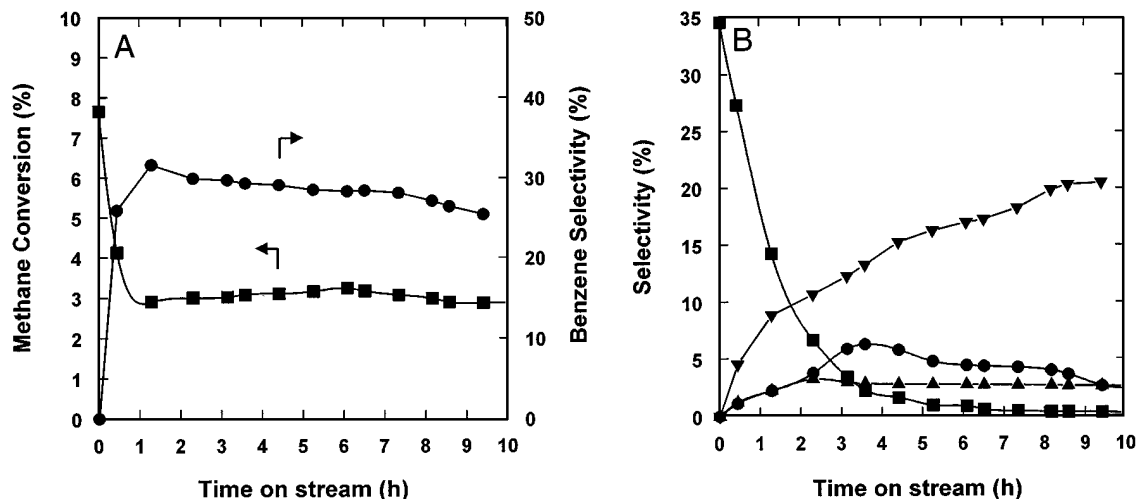


FIG. 1. (A) Methane conversion and benzene selectivity and (B) selectivities toward CO (■), naphthalene (●), toluene (▲), and C<sub>2</sub>-C<sub>3</sub> hydrocarbons (▼) for CH<sub>4</sub> reaction over 2 wt% V/H-ZSM-5 prepared by impregnation and prerduced at 500°C for 6 h in CO. The catalytic reaction was conducted at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>.

a benzene selectivity of about 30% at a CH<sub>4</sub> conversion of 3.2% was achieved. During the first 20 min on-stream, virtually no hydrocarbon products were formed, and the major gas-phase products were CO, CO<sub>2</sub>, and H<sub>2</sub>O. The amount of CO gradually decreased with increasing time-on-stream and was almost totally absent after 4 h of reaction. In addition to benzene, naphthalene, and toluene were formed, but with lower selectivities. The selectivity of naphthalene reached a value of 6% immediately following the initial activation period, but then declined slowly with increasing time-on-stream. For toluene, a maximum selectivity of 3% was observed. Thus, after a sufficiently long reaction time, mainly benzene, and some toluene and naphthalene was produced, and the maximum selectivity toward aromatic

hydrocarbons was higher than 36%. On the other hand, the selectivity toward C<sub>2</sub>-C<sub>3</sub> hydrocarbons (mainly ethylene) increased continuously with increasing reaction time, as coke deposition gradually deactivated the acidic sites in the zeolite, where the ethylene undergoes secondary reaction. The formation of coke was confirmed by evaluating the carbon mass balance during methane activation.

## 2. Effect of Catalyst Preparation

Catalysts prepared by solid state ion exchange always had a lower catalytic activity (Table 2), and, because of experimental uncertainty, a more erratic selectivity pattern than those prepared by impregnation. This is illustrated by comparing the results of Fig. 1 with those of Fig. 2, which were

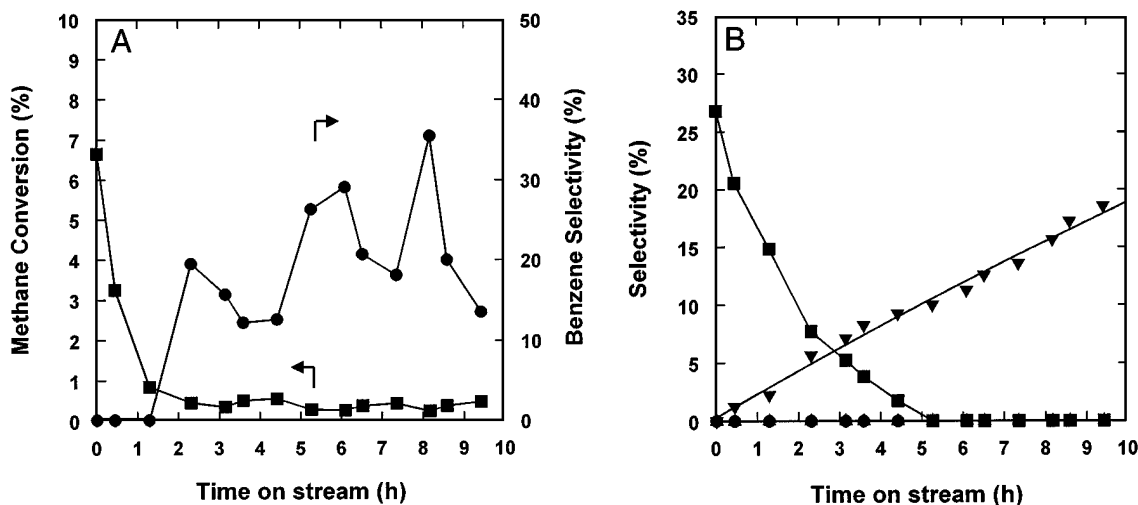


FIG. 2. (A) Methane conversion and benzene selectivity and (B) selectivities toward CO (■), naphthalene (●), toluene (▲), and C<sub>2</sub>-C<sub>3</sub> hydrocarbons (▼) for CH<sub>4</sub> reaction over 2 wt% V/H-ZSM-5 prepared by solid state ion exchange and prerduced at 500°C for 6 h in CO. The catalytic reaction was conducted at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>.

obtained for a 2 wt% V/H-ZSM-5 catalyst that had been prepared by solid state ion exchange. Following an initial activation period, a benzene selectivity ranging between 13 and 36% at a methane conversion of 0.6% was achieved. No toluene and naphthalene were formed during methane activation, suggesting that higher aromatic compounds, such as naphthalene cannot be formed in the partially blocked zeolite channels. Indeed, solid state ion exchange may lead to some local lattice destruction (16, 17), which can prevent the formation of the larger naphthalene within the zeolite channels. In addition to benzene, C<sub>2</sub>–C<sub>3</sub> hydrocarbons were produced, and the selectivity towards these products increased continuously with increasing reaction time.

The lower methane conversion over the solid state ion-exchanged materials can be explained by comparing the hydroxyl region of the zeolites, as measured by FT-IR spectroscopy. As an example, we will discuss in detail the 2 wt% V/H-ZSM-5 zeolites, prepared by both impregnation and solid state ion exchange; however, similar results were obtained for the other catalytic systems. The parent H-ZSM-5 material possessed three distinguishable hydroxyl bands after calcination. One of these, having a vibrational frequency of 3610 cm<sup>-1</sup>, is associated with the Brønsted acidity of the zeolite (21–23). A second hydroxyl group, having a stretching frequency of 3745 cm<sup>-1</sup>, has been attributed to silanol groups that terminate the zeolite lattice. These hydroxyl groups are predominantly located at the outer surface of the zeolite (21, 22). A weaker band at around 3670 cm<sup>-1</sup> is due to hydroxyl groups that are associated with extra-framework aluminum species (24). Addition of 2 wt% vanadium, followed by calcination, resulted in an overall decrease in amplitudes of the hydroxyl bands of the zeolite material; however, the relative intensity decrease of the three hydroxyl groups was dependent on the preparation method. In the case of solid state ion-exchanged materials, the bands at 3610 and 3670 cm<sup>-1</sup> were strongly affected, while for the impregnated samples, predominantly the intensity of the 3745 cm<sup>-1</sup> band decreased. Thus, in samples prepared by impregnation, vanadium preferentially reacts with the silanol groups at the outer surface of the zeolite. Materials prepared by solid-state ion exchange, on the other hand, did not possess many Brønsted acid sites after calcination. This is due to the reaction of vanadium chloride with the Brønsted acid sites during preparation to form the cation at the exchange site plus some gas phase HCl. As a consequence, the differences in catalytic activity/selectivity between impregnated and solid state ion-exchanged materials can be explained in terms of differences in zeolite acidity and the state of the transition metal ion. In the case of solid state ion-exchanged zeolites, the metal ions were predominantly located in the zeolite channels at ion exchange sites. For catalysts prepared by impregnation, the transition metal ions were preferentially anchored at the outer surface, probably as small clusters or a thin film of the ox-

ide, and only a fraction diffused into the zeolite channels where they replaced the protons at Brønsted acid sites.

### 3. Effect of Catalyst Pretreatment

The results of Table 2 also show that methane activation was strongly influenced by catalyst prereduction, and that CO-prereduced catalysts were always the most active materials, except for Fe/H-ZSM-5 prepared by impregnation, for which pretreatment in CO did not improve the activity. This is nicely illustrated by considering the catalytic performance of solid state ion-exchanged Fe/H-ZSM-5 catalysts. As indicated in Table 2, this material possessed almost no catalytic activity prior to CO treatment. Only after prereducing the catalyst with CO at 500°C, was a benzene selectivity of more than 40% achieved at a methane conversion of about 3.9%.

The effect of CO reduction is further illustrated in Fig. 3, which describes the results obtained during a catalytic reaction for 4 h at 750°C over a nonprereduced solid state ion-exchanged 2 wt% Fe/H-ZSM-5 catalyst. The methane activity decreased to zero after 4 h on-stream, and no benzene formation was detected for a period up to 10 h. The sample was then cooled to 500°C and treated with CO for 6 h. After this treatment step, the catalyst was again heated to 750°C in a flow of helium, and then subjected to methane for 10 h. After an initial activation period of about 2 h, a benzene selectivity of 42% was reached at a methane conversion of 4.1%. During the first 30 min on stream, no benzene was detected, and the major gas-phase products were CO, CO<sub>2</sub>, and H<sub>2</sub>O. In addition to benzene, C<sub>2</sub>–C<sub>3</sub> hydrocarbons, mainly ethylene, were formed. However, neither naphthalene nor toluene were detected. After a sufficiently long reaction time, the methane conversion and

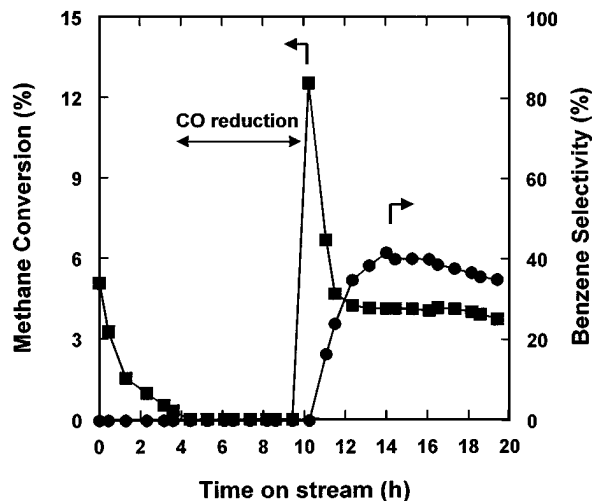


FIG. 3. Methane conversion and benzene selectivity results for CH<sub>4</sub> reaction over 2 wt% Fe/H-ZSM-5 prepared by solid state ion exchange. The catalytic reaction was at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>.

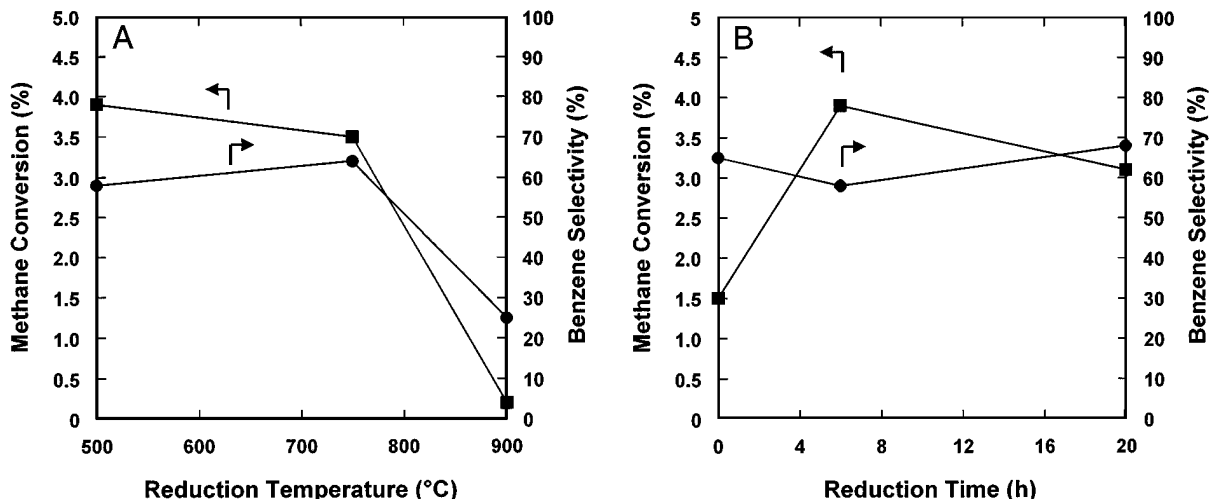


FIG. 4. (A) Effect of reduction temperature and (B) reduction time on the conversion of methane over 2.0 wt% Fe/H-ZSM-5 prepared by impregnation. The catalytic reaction was at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>. For experiment A, the reduction time was 6 h, whereas the reduction temperature was 500°C for experiment B.

benzene selectivity decreased, while the selectivity toward C<sub>2</sub>-C<sub>3</sub> hydrocarbons increased continuously with increasing reaction time. Thus, catalytically inactive materials can be made active by pretreating the catalyst with CO. This observation suggests that CO treatment, although necessary to reduce the metal ion to the catalytically active state, also influences the dispersion of the transition metal ion. As will be shown in part II of this study (18), CO treatment at high temperature resulted in an enrichment of the transition metal ion at the outer surface of the zeolite. The water produced during the early states of the subsequent reaction with CH<sub>4</sub> must reintroduce Brønsted acid sites into the ion-exchanged material.

The time and temperature of reduction are also important, as illustrated in Fig. 4. This figure shows that increasing the reduction temperature to 750°C resulted in a slight increase in benzene selectivity; however, both the activity and selectivity decreased significantly at higher reduction temperatures. Almost no methane conversion was observed after reducing the catalyst for 6 h at 900°C. This must be due to carbon deposition via the Boudouard reaction. It is also important to stress that higher reduction temperatures resulted in a shortening of the initial induction time for catalysts prepared by impregnation.

In another series of experiments, the effects of calcination temperature and reaction temperature on the catalytic performance of 0.6 wt% Fe/H-ZSM-5 catalysts were studied. The results are shown in Figs. 5 and 6. It is clear from Fig. 5 that a reasonably constant conversion could be obtained by calcining the catalysts between 500 and 700°C in oxygen. Calcination temperatures at 900°C, however, resulted in a catalytically inactive material. This deactivation must be due to lattice destruction and/or thermal condensation of Brønsted acid sites. This has recently been proven

for Mo/H-ZSM-5 catalysts by Liu *et al.* (25). The methane conversion increased with increasing reaction temperature (Fig. 6), but the selectivity for benzene decreased below 40% at a reaction temperature of 800°C. At higher reaction temperatures, hydrocarbons partially converted to coke. Thus, methane activation becomes less selective at higher reaction temperatures, which is disappointing because the equilibrium conversion of methane to aromatics increases with increasing temperature (14).

The methane conversion and the selectivity toward benzene increased with decreasing space velocity of methane as shown in Fig. 7. At a gas hourly space velocity (GHSV)

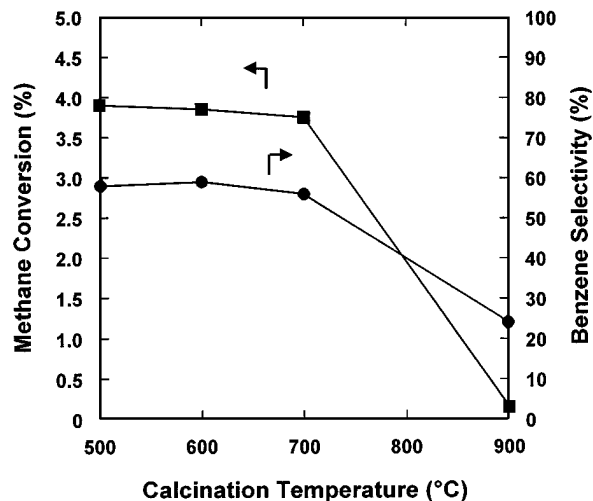


FIG. 5. Effect of calcination temperature on CH<sub>4</sub> activation over 0.6 wt% Fe/H-ZSM-5 prepared by impregnation and prereduced at 500°C for 6 h in CO. The catalytic reaction was at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>.

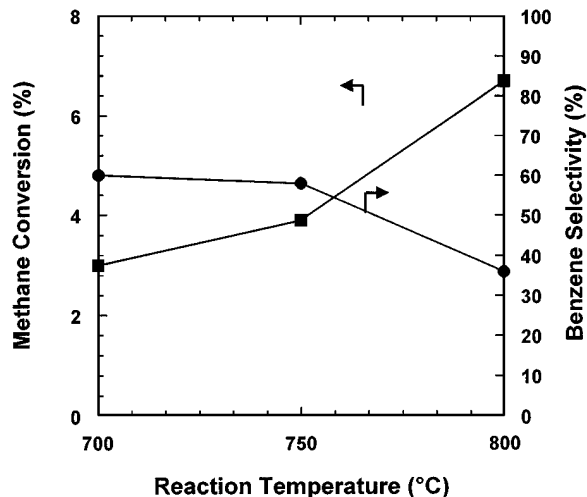


FIG. 6. Effect of reaction temperature on the conversion of methane over 0.6 wt% Fe/H-ZSM-5 prepared by impregnation and prerduced at 500°C for 6 h in CO. The catalytic reaction was at 1 atm and GHSV = 800 h<sup>-1</sup>.

of 400 h<sup>-1</sup>, a benzene selectivity of 70% at a methane conversion of about 6.8% was achieved over a 0.6 wt% Fe/H-ZSM-5 catalyst. Furthermore, the selectivity toward C<sub>2</sub>-C<sub>3</sub> hydrocarbons, mainly ethylene, decreased with decreasing space velocity. This implies that ethylene is the initial product of methane activation and, that aromatics, such as benzene, are formed by subsequent reaction of ethylene, as described previously (14).

#### 4. Effect of Zeolite Acidity

The effect of the number of Brönsted acid sites on methane activation over 2 wt% Cr/H-ZSM-5 zeolites was studied by preparing zeolite materials differing in their

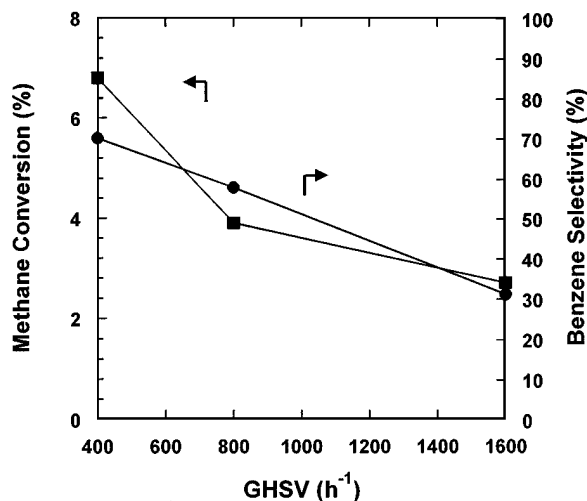


FIG. 7. Effect of GHSV on the conversion of methane over 0.6 wt% Fe/H-ZSM-5 prepared by impregnation and prerduced at 500°C for 6 h in CO. The catalytic reaction was at 750°C and 1 atm.

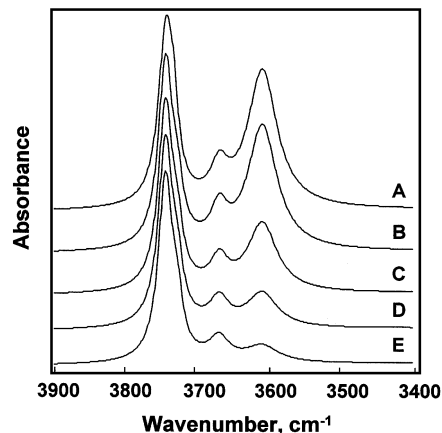


FIG. 8. Infrared spectra of 2 wt% Cr/H-ZSM-5 zeolites that contained different concentrations of Brönsted acid sites. Samples were prepared by ion exchange in 1 M solutions containing (A) NH<sub>4</sub>NO<sub>3</sub>, (B) 5:1 NH<sub>4</sub>NO<sub>3</sub>:NaCl, (C) 3:1 NH<sub>4</sub>NO<sub>3</sub>:NaCl, (D) 2:1 NH<sub>4</sub>NO<sub>3</sub>:NaCl, and (E) NaCl. Materials were subsequently impregnated with CrO<sub>3</sub>, dried and calcined at 500°C for 5 h.

Na<sup>+</sup>:H<sup>+</sup> ratio, and consequently, in their number of Brönsted acid sites. The number of Brönsted acid sites, expressed as a percentage relative to a fully exchanged H-ZSM-5 zeolite, was determined by measuring the intensity of the 3610 cm<sup>-1</sup> band of the calcined catalyst from the FT-IR spectra shown in Fig. 8. The number of Brönsted acid sites, together with the methane conversion and benzene selectivity, is given in Fig. 9. It is clear that methane conversion and benzene selectivity were close to zero if the zeolite material had almost no Brönsted acid sites. Furthermore, an increasing number of Brönsted OH-groups resulted in a gradual increase in methane conversion and benzene formation, and the Cr/H-ZSM-5 catalyst without any added

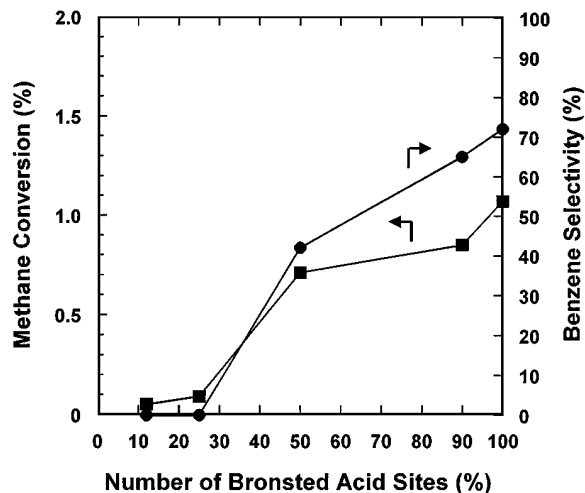


FIG. 9. Effect of the number of Brönsted acid sites on CH<sub>4</sub> activation over 2 wt% Cr/H-ZSM-5 prepared by impregnation and prerduced at 500°C for 6 h in CO. The catalytic reaction was at 750°C, 1 atm, and GHSV = 800 h<sup>-1</sup>.

sodium possessed a maximum benzene selectivity of 72% at a conversion of 1.1%. The present observations, together with results of a previous study in which we have shown that ethylene can be converted over Mo/H-ZSM-5 zeolites (13), confirm the crucial role of acid sites in methane activation. The Brönsted acid sites are responsible for oligomerizing and converting the initially formed ethylene into benzene, toluene, and naphthalene. By doing so, the acid sites shift the thermodynamically unfavorable equilibrium for the formation of ethylene to a more favorable equilibrium for the formation of aromatics. Wang *et al.* (5) also observed this effect by studying Mo/H-ZSM-5 zeolites with different Si:Al ratios. They found an increase in methane conversion with decreasing Si:Al ratio, i.e., with an increasing number of Brönsted acid sites.

### 5. Effect of Metal Loading

The catalytic performances are not only determined by the preparation and treatment conditions, and by the zeolite acidity, but also by the overall amount of transition metal ions. As an example, we will discuss the Cr/H-ZSM-5 system in more detail. Similar results were observed for other transition metal ions, although the exact optimum metal loading is dependent on the transition metal ion (e.g., around 4 wt% for Mo). The effect of the Cr loading on the methane activation and benzene selectivity is given in Fig. 10. It is clear that maximum catalytic activity was obtained at around 2 wt% and that higher Cr loadings did not result in more active materials. However, the selectivity toward benzene gradually increased with increasing Cr loading and leveled off at the highest Cr loading, i.e., 6 wt%. It is important to note here that the highly loaded materials, prepared by impregnation, contained Brönsted acid sites, as indicated by FT-IR spec-

troscopy. This suggests that there are still enough Brönsted acid sites available to convert the initially formed ethylene to aromatic compounds.

One can speculate as to why the methane conversion goes through a maximum. The most likely hypothesis is that the dispersion of the active  $\text{CrO}_x$  phase decreases with increasing Cr loading. Indeed, detailed spectroscopic investigations of extensively loaded Cr-zeolites show a low  $\text{Cr}^{n+}$  dispersion, as indicated by the formation of  $\alpha\text{-Cr}_2\text{O}_3$  (26). Another possible reason is lattice destruction. Pearce and Mortier (27) have shown by XRD that the introduction of  $\text{Cr}^{3+}$  in zeolites A and X resulted in lattice destruction, especially at higher Cr loadings. Recently, Liu *et al.* (25) concluded from detailed NMR studies on Mo/H-ZSM-5 catalysts that the extractability of framework Al by Mo species increases with increasing Mo loading. The extraction process leads to the formation of nonframework Al at first, and then to the formation of a new crystalline phase of  $\text{Al}_2(\text{MoO}_4)_3$ . These materials were always catalytically inferior for methane activation.

Another interesting observation is that the induction time for the Cr/H-ZSM-5 materials decreased with increasing Cr loading, independent of the treatment and preparation condition. It is known that increasing Cr loading results in an increase of the polychromate:monochromate ratio on the zeolitic surfaces and that surface polychromates are more readily reducible than surface monochromates (26). In other words, the shorter induction times can be explained in terms of differences in redox behavior of supported  $\text{CrO}_x$ .

## CONCLUSIONS

1. Mo-, Fe-, V-, W-, and Cr-loaded H-ZSM-5 zeolites are able to selectively convert methane to aromatics, and the activity decreased in the order: Mo (18.3) > W(10.8) > Fe (5.7) > V (3.9) > Cr (1.5), where the numbers in parentheses are the rates of methane reaction (molec. reacted/metal atom/h) obtained after 3 h on-stream.

2. The induction period, prior to the formation of benzene, toluene, and naphthalene, decreases with increasing metal ion loading.

3. The catalytic activity is directly proportional to the number of Brönsted acid sites. These sites are responsible for the oligomerization and dehydrocyclization of the primary ethylene product.

4. The catalytic performance is strongly dependent on the preparation method, the treatment condition, and the metal loading. The activity of catalysts prepared by impregnation is always higher than that of solid state ion-exchanged materials. Furthermore, inactive materials were made active by pretreatment with CO. Optimum activity was obtained for 2–4 wt% TMI/H-ZSM-5 materials. The state of the metal, as determined by X-ray photoelectron

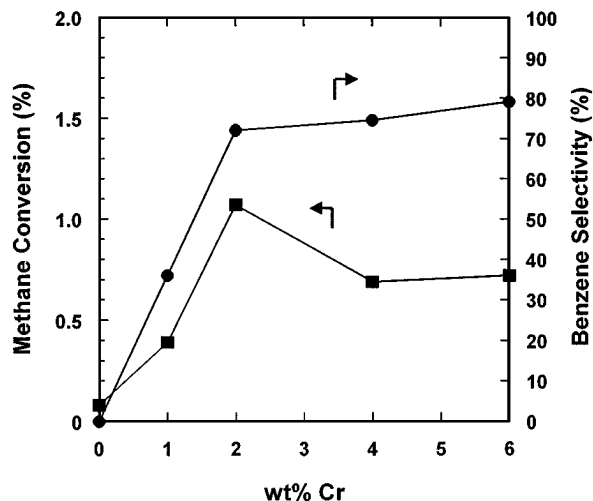


FIG. 10. Effect of Cr loading on  $\text{CH}_4$  activation and benzene selectivity over Cr/H-ZSM-5 prepared by impregnation and prerduced at  $500^\circ\text{C}$  for 6 h in CO. The catalytic reaction was at  $750^\circ\text{C}$ , 1 atm, and  $\text{GHSV} = 800 \text{ h}^{-1}$ .



spectroscopy, will be described more fully in part II of this study.

5. The supported transition metal ions are predominantly located in the zeolite channels of solid state ion materials. These materials have only a small amount of Brönsted acidity. For samples prepared by impregnation, the supported transition metal ions are mainly located at the outer surface, and only a fraction diffuses into the channels of the zeolite material.

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