JOURNAL OF CATALYSIS **175,** 347–351 (1998)
ARTICLE NO. CA982011

RESEARCH NOTE

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

II. Catalyst Characterization by X-Ray Photoelectron Spectroscopy

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Received September 9, 1997; revised December 29, 1997; accepted January 16, 1998

X-ray photoelectron spectroscopy (XPS) has been used to determine the state of the transition metal ions (V, Cr, Fe, W, and Mo) on impregnated and ion-exchanged H-ZSM-5 zeolites that are active for the catalytic conversion of methane to benzene at 750°C. During an induction period, transition metal suboxides are formed on all of the impregnated catalysts except Mo/H-ZSM-5 for which Mo_2C is formed. Ion-exchanged samples became more active after treatment with CO at 500°C. For the Fe/H-ZSM-5 sample, this treatment resulted in the migration of the metal to the external surface of the zeolite and the formation of an iron oxide phase.

Recent studies have demonstrated that methane can be selectively converted to aromatics in the absence of oxygen over several transition-metal-ion-supported H-ZSM-5 zeolites (1–9). Ethylene, which is the primary product of methane activation, undergoes subsequent oligomerization and cyclization reactions on Brönsted acid sites of the zeolite to form aromatics, such as benzene, naphthalene, and toluene. Many studies have been devoted to the spectroscopic characterization of Mo/H-ZSM-5 catalysts, and various phases, e.g., oxides, suboxides, and carbides, have been proposed in the literature as the material responsible for initial activation of methane (2–7). Recent characterization studies, however, have clearly demonstrated that exposure of a calcined Mo/H-ZSM-5 catalyst to CH_4 at high temperature causes a reduction of molybdenum oxide to the carbide, Mo_2C, which was identified by X-ray photoelectron spectroscopy (5–7). The disappearance of Mo^{6+} and the formation of Mo_2C were virtually complete after exposure of the calcined catalysts to CH_4 for 2 h, which corresponds to the time of the initial induction period of these materials. Furthermore, pretreatment of the catalyst in a CH_4/H_2 gas mixture resulted in the formation of Mo_2C, and almost eliminated the induction period, confirming that Mo_2C is the active phase in methane activation (7).

We have recently shown (8, 9) that Fe/H-ZSM-5, V/H-ZSM-5, W/H-ZSM-5, and Cr/H-ZSM-5 catalysts are also able to activate methane in the absence of oxygen, and their performances are strongly dependent on preparation and treatment conditions. However, no detailed spectroscopic characterization studies of these catalytic materials have appeared previously in the literature. In this note, X-ray photoelectron spectroscopy (XPS) has been used to identify the active phases for methane conversion, and the results are compared with those obtained for Mo/H-ZSM-5 catalysts. It will be shown that different phases, depending on the metal, are able to activate methane in the absence of oxygen.

Two wt% Fe/H-ZSM-5, V/H-ZSM-5, W/H-ZSM-5, Cr/H-ZSM-5, and Mo/H-ZSM-5 catalysts were prepared starting from commercial H-ZSM-5 (PQ Corp., CBV 5020E) having a Si/Al ratio of 25. Details of preparation and treatment conditions can be found in part I of this study (9).

X-ray photoelectron spectra were acquired using a Perkin-Elmer (PHI) Model 5500 spectrometer. All spectra were obtained using samples prepared in the form of pressed wafers. These samples were treated in different reactant gases in a specially designed fused-quartz reactor system with an O-ring-sealed port that allowed *in situ* transfer of the ceramic holder containing the treated sample into a stainless steel vacuum transport vessel (PHI Model 609217). The removable vessel was then transferred to a similar port on the inlet system of the spectrometer, which was subsequently evacuated, allowing the sample to be introduced into the analysis chamber of the instrument using

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0021-9517/98 $25.00

magnetically coupled transfer rods without exposure to the air. XPS data were typically acquired using a pass energy of 29.25 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. All binding energies were referenced to the zeolitic Al 2p and Si 2p lines at 74.5 and 102.8 eV, respectively.

The reactant gases, which included 10% N_2/CH_4 (UHP), O_2 (UHP), He (UHP), and CO (UHP), were obtained from Matheson. When CO was used, traces of iron carbonyls were removed by flowing the CO through an alumina tube filled with quartz chips at 300°C. The other gases were used without further purification. Gas flows were regulated by mass flow controllers (MKS Model 1159A). In the quartz reactor system, the catalyst was calcined in flowing O_2 for 1 h at 500°C, and flushed in He at 500°C for 30 min (flow rate of 50 ml/min). The calcined sample was then transferred to the XPS spectrometer for spectral measurements. In another series of experiments, calcined catalysts were subjected to a CH_4 stream at 750°C for different time periods. The treated samples were then transferred to the spectrometer, and the spectra were obtained.

The chemical state of the transition metal ions (TMI's) and of carbon in the 2 wt% TMI/H-ZSM-5 catalysts, prepared by impregnation, were examined by XPS. All experiments were designed to simulate the conditions applied in the catalytic reactions, described in part I of this study (9). Here it is assumed that the porous pressed wafers used in the XPS experiments behaved in the same manner with respect to CH_4 and CO exposure as the catalyst bed. The XPS binding energies (BE) and sample colors after various times on stream are summarized in Table 1. The observed XPS BE's can be assigned to certain oxidation states by comparison with BE's of relevant reference compounds, which are given in Table 2.

The spectra obtained in the Mo 3d region and C 1s region of a 2 wt% Mo/H-ZSM-5 catalyst for increasing time-on-stream were discussed in detail in previous publications (5–7). It is sufficient to note that Mo_2C, characterized by Mo 3d BE values at 227.9 and 231.1 eV, and by a C 1s BE value at 282.7 eV, was formed during initial methane activation. Increasing time-on-stream resulted in an increasing amount of coke, which partially covered both the active Mo_2C phase and the zeolite material.

The spectra obtained in the Fe 2p region of a 2 wt% Fe/H-ZSM-5 catalyst are given in Fig. 1. The calcined material was orange-colored, and was characterized by Fe $2p_{3/2}$ and Fe $2p_{1/2}$ BE's of 711 and 724 eV, respectively, as shown in spectrum A. The spin-orbit splitting was 13 eV. These observations are consistent with supported Fe_2O_3 (Table 2). A weak shake-up peak is not observed because of the relatively small signal-to-noise ratio. After flowing methane over the catalyst for 3.5 h at 750°C, the slightly less intense Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks remained at 711 and 724 eV, respectively (spectrum B). Although the XPS evidence for the reduction of Fe_2O_3 to Fe_3O_4 is ambiguous because of the similarities in the binding energies, no peak was observed at ca. 707 eV, which would indicate the formation of an Fe_xC phase. EPR measurements showed that a broad signal with

TABLE 1

Color and XPS Binding Energies (eV) of 2.0 wt% Transition Metal Ion-loaded ZSM-5 Zeolites during Methane Conversion at 750°C[a]

Transition metal ion (spin-orbit splitting level)	Time-on-stream (h)	Color	XPS BE (eV) of TMI	C 1s BE (eV)
Mo ($3d_{5/2}$)	0	white-yellow	233.1 (m)	284.6 (w)
	3.5	black	227.9 (m)	284.6 (sh); 283.5
	10	black	227.9 (m)	283.5 (s)
Fe ($2p_{3/2}$)	0	yellow-orange	711 (m)	284.6 (m, br)
	3.5	black	711 (m)	283.5 (s)
	10	black	711 (w)	283.5 (w)
V ($2p_{3/2}$)	0	light-yellow	517.4 (s)	284.6 (w)
	3.5	gray-blue	515.7 (m, br)	283.6 (w)
	10	black	515.7 (w, br)	283.2 (s)
Cr ($2p_{3/2}$)	0	yellow	577.9 (s)	284.5 (br)
	3.5	gray-green	576.1 (s)	284.3 (s)
	10	black	576.1 (w)	283.5 (br); 284.2 (sh)
W ($4f_{7/2}$)	0	white-yellow	35.5 (br)	284.6 (w)
	2	blue	35.5 (s)	284.2 (w)
	6	black	35.5 (s)	283.2 (m); 284.2 (sh)
	13	black	35.5 (br); 33.5 (sh)	283.2 (s)
	24	black	35.5 (s); 33.5 (m, br)	283.5 (s)

[a] s, strong; m, medium; w, weak; sh, shoulder; br, broad.

TABLE 2

Literature Values of XPS Binding Energies (eV) for Mo, Fe, V, Cr, and W

TMI (atomic level)	Compound (valence state of metal ion)	XPS BE (eV)	Reference
Mo ($3d_{5/2}$)	MoO_3 (VI)	232.6–233.0	7, 10, 11
	H_xMoO_3 (V)	231.4	
	MoO_2 (IV)	229.4–230.0	
	Mo (0)	227.8–227.9	
	Mo_2C	227.8–228.4	7, 12
Fe ($2p_{3/2}$)	Fe_3O_4 (II, III)	710.5–711.2	10, 13, 14
	Fe_2O_3 (III)	711.1 with shake-up peak	
	FeO (II)	709.9	
	Fe (0)	706.8	
	Fe_xC	707.0	15
V ($2p_{3/2}$)	V_2O_5 (V)	517.4	10, 16, 17
	VO_2 (IV)	516.3	
	V_2O_3 (III)	515.7	
	V (0)	512.2	
Cr ($2p_{3/2}$)	CrO_3 (VI)	578.3–580	10, 18
	Cr_2O_3 (III)	576.8–577	
	Cr (0)	574.3–576.4	
W ($4f_{7/2}$)	WO_3 (VI)	35.5–36.1	10, 11, 19–21
	WO_2 (IV)	32.4–32.8	
	W (0)	30.8–31.3	
	WC	31.4–32.0	

$g = 2.06$ and a peak-to-peak width of 600 G was formed when the sample was treated in CH_4 (14). This signal has been assigned to small Fe_3O_4 clusters (14).

In part I of this study (9), it was shown that the catalytic performances of 2 wt% TMI/H-ZSM-5 zeolites for methane conversion to aromatics were strongly influenced by their preparation and treatment conditions. First, the catalytic activities of impregnated samples were always higher than those of corresponding solid state ion-exchanged materials. Second, catalytically inactive materials could be made active by pretreatment with CO at 500°C for 6 h. As will be shown below, these differences in activity are related to differences in the location of the TMI's.

The spectrum in the Fe 2p region of 2 wt% Fe/H-ZSM-5 catalyst, prepared by solid state ion exchange (Fig. 1, spectrum C) was very weak compared to that of the impregnated sample (spectrum A). Thus, a large fraction of the iron ions diffused into the channels of the zeolite material during solid state ion exchange. For samples prepared by impregnation, however, Fe_2O_3 was mainly located at the outer surface of the zeolite material and only a fraction diffused into the zeolite channels. Further support for these differences in TMI distribution comes from FT-IR measurements which were presented in part I of this study. It was shown that materials prepared by solid state ion exchange possessed few Brönsted acid sites after calcination. This is due to the reaction of the metal chloride with the Brönsted acid sites during preparation to form the cation at the exchange site and to release gas phase HCl. On the other hand, in samples prepared by impregnation, the metal ion preferentially reacts with the silanol groups at the outer surface of the zeolite, and the Brönsted acid sites are not significantly affected.

We also studied the influence of the pretreatment conditions on the distribution of Fe in 2 wt% Fe/H-ZSM-5 catalysts, prepared by solid state ion exchange. As shown in part I, the freshly prepared materials were inactive for methane conversion, and only became active after pretreating the samples in CO for 6 h at 500°C. Treating the ion-exchanged catalyst at 750°C for 4 h in methane did not change the spectrum; the corresponding Fe signals remained weak as shown in Fig. 1, spectrum D. In strong contrast, the spectrum of the CO-treated material was characterized by much larger Fe peaks at around 711 and 724 eV (spectrum, E). Thus, after CO treatment a large fraction of the iron oxide was located at the outer surface of the zeolite material, and became available for methane activation.

The spectra of Fig. 2 were obtained in the V 2p region for a 2 wt% V/H-ZSM-5 catalyst prepared by impregnation. The calcined catalyst was light yellow, and the corresponding XPS spectrum was characterized by a V $2p_{3/2}$ peak at 517.4 eV (Fig. 2, spectrum A). This BE is typical for V_2O_5 (Table 2); however, the presence of some V(IV) cannot be excluded. Indeed, ESR measurements indicated the presence of traces of V(IV). The intense peak at around

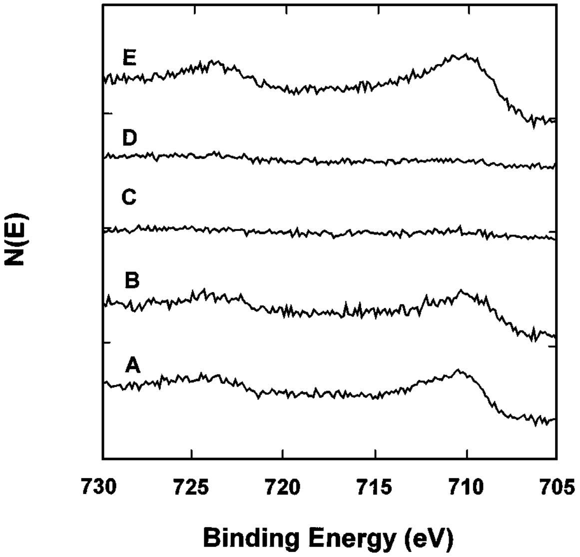

FIG. 1. XPS spectra in the Fe 2p region of 2 wt% Fe/H-ZSM-5 catalysts: (A) prepared by impregnation, after calcination at 500°C for 1 h; (B) prepared by impregnation, after methane activation at 750°C for 3.5 h; (C) prepared by ion exchange, after calcination at 500°C for 1 h; (D) prepared by ion exchange, after methane activation at 750°C for 4 h; (E) prepared by ion exchange, after CO treatment at 500°C for 6 h.

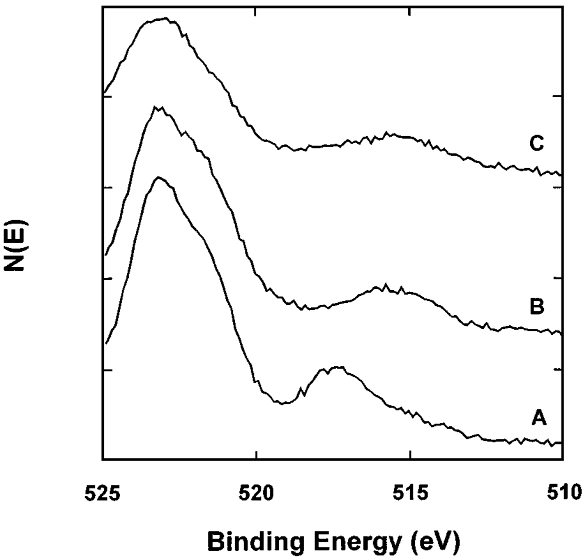

FIG. 2. XPS spectra in the V 2p region of 2 wt% V/H-ZSM-5 catalysts prepared by impregnation: (A) after calcination at 500°C for 1 h; (B) after methane activation at 750°C for 3.5 h; and (C) after methane activation at 750°C for 10 h.

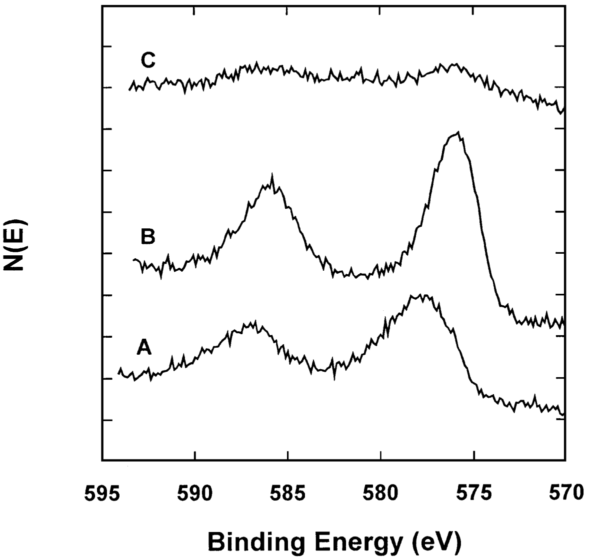

FIG. 3. XPS spectra in the Cr 2p region of 2 wt% Cr/H-ZSM-5 catalysts prepared by impregnation: (A) after calcination at 500°C for 1 h; (B) after methane activation at 750°C for 3.5 h; and (C) after methane activation at 750°C for 10 h.

523 eV is an O 1s X-ray satellite peak, which overshadowed the V $2p_{1/2}$ peak of V_2O_5 located at around 525 eV. Treating the catalyst with methane at 750°C for 3.5 h resulted in a change in color to gray-blue. The resulting V $2p_{3/2}$ peak was located at 515.7 eV (spectrum B), which is typical for V_2O_3 (Table 2). The same peak position was observed for the catalyst treated for 10 h in methane; however, the peak intensity was less (spectrum C) and the material was black. The corresponding C 1s region showed an intense peak (spectrum not shown) centered at around 283.2 eV, which is due to coke formation. Thus, the active V_2O_3 phase was partially covered by coke after 10 h on-stream.

The spectra obtained in the Cr 2p region of an impregnated 2 wt% Cr/H-ZSM-5 catalyst for increasing time-on-stream are shown in Fig. 3. The Cr 2p region shows that after calcination, Cr(VI) was the main species in the yellow-colored catalyst, although some traces of Cr(V) were detected by ESR. After reaction with methane for 3.5 h, the Cr $2p_{3/2}$ peak shifted from 577.9 to 576.1 eV, which is close to the value for Cr_2O_3. The spin-orbit splitting was 9.7 eV, which is also typical for Cr_2O_3 (10). However, it is important to note here that XPS is often found to be inconclusive in distinguishing between Cr(III) and Cr(II) because of the small differences in BE's (18). Further evidence for the presence of supported Cr_2O_3 comes from ESR measurements, which showed the presence of a broad isotropic signal centered around $g = 1.97$. This signal is due to Cr_2O_3 clusters (18). After reaction for 10 h, there was a significant decrease in the intensity of the Cr 2p peaks. Meanwhile, the C 1s signal (spectrum not shown) shifted to a lower binding energy and decreased in intensity. The lower binding energy indicates a transition to coke, which may have partially covered the Cr_2O_3 clusters, but simultaneously the Cr_2O_3 clusters may have increased in size.

The spectra obtained in the W 4f region for a 2 wt% W/H-ZSM-5 catalyst are shown in Fig. 4. The white-yellow sample, obtained after calcination, was characterized by

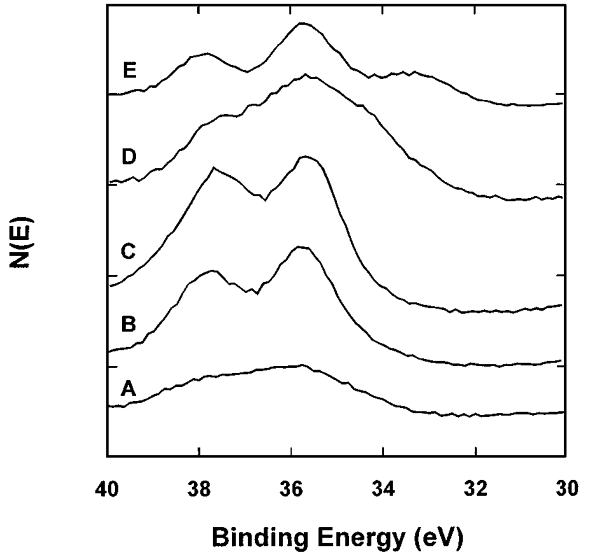

FIG. 4. XPS spectra in the W 4f region of 2 wt% W/H-ZSM-5 catalysts prepared by impregnation: (A) after calcination at 500°C for 1 h; (B) after methane activation at 750°C for 2 h; and (C) after methane activation at 750°C for 6 h; (D) after methane activation at 750°C for 13 h; and (E) after methane activation at 750°C for 24 h.

W $4f_{7/2}$ and W $4f_{5/2}$ peaks located at ca. 35.5 and 38 eV, respectively. These BE's are typical for the presence of supported WO_3 (Table 2). After flowing methane over the catalyst for 2 h at 750°C, the color of the catalyst was blue. The corresponding XPS spectrum in the W 4f region was better resolved and more intense than that of the calcined sample, which suggests a change in W dispersion. The BE's were slightly shifted to lower energy, which could indicate a partial reduction to W(V). After 6 h on-stream, the catalyst turned black, and a C 1s signal of coke at 283.2 eV was observed. The XPS spectrum in the W 4f region of a catalyst treated in methane for 13 h showed an additional shoulder at around 33.5 eV, which became fully resolved after 24 h on-stream. This peak at 33.5 eV is attributed to the presence of WO_2 (Table 2), although the observed BE is somewhat greater than that for WO_2 reported in the literature. There was no XPS evidence for the formation of WC. Thus, during methane activation WO_3 was partially reduced to WO_2. The slow rate of reduction is consistent with the increase in CH_4 conversion that occurred over several hours on-stream.

The XPS results in Figs. 1–4 show unambiguously that neither reduced metals nor metal carbides are formed on Fe/H-ZSM-5, V/H-ZSM-5, Cr/H-ZSM-5, and W/H-ZSM-5 catalysts during methane activation. This is significant because the presence of Mo_2C was confirmed by XPS for Mo/H-ZSM-5 catalysts (7). Thus, different phases are able to activate methane at high temperatures in the absence of oxygen. The active phase depends on the particular transition metal that is present on the zeolite. In particular, for the respective elements, it appears that the active suboxide phases are Fe_3O_4, V_2O_3, Cr_2O_3, and WO_2 located on the external surface of the zeolite. The enhanced catalytic activity of the ion-exchanged samples upon CO-treatment (part I) may result from the migration of the metal ions from ion exchange sites to the external region of the zeolite crystallites. This migration was demonstrated for Fe/H-ZSM-5, and it presumably occurs with the other catalysts except V/H-ZSM-5, for which no catalytic enhancement was observed.

ACKNOWLEDGMENTS

This work was sponsored by the National Science Foundation under Grant CHE-9520806. B.M.W. is a postdoctoral research fellow of the Belgian National Fund of Scientific Research.

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