Study of W/HZSM-5-based catalysts for dehydro-aromatization of CH_4 in absence of O_2.
I. Performance of catalysts [*]

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With incorporation of Zn (or Mn, La, Zr) into the W/HZSM-5 catalyst, highly active and heat-resisting W/HZSM-5-based catalysts were developed and studied. Under reaction conditions of 0.1 MPa, 1073 K, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}, the conversion of methane reached 18–23% in the first 2 h of reaction, and the corresponding selectivity to benzene, naphthalene, ethylene and coke was 56–48, $\sim$18, $\sim$5 and $\sim$22%, respectively. Addition of a small amount of CO_2 ($\leqslant$2%) to the feed-gas was found to significantly enhance the conversion of methane and the selectivity of benzene, and to improve the performance of coke-resistance of the W/HZSM-5-based catalysts. Heavy deposition of carbon on the surface of the functioning catalyst was the main reason leading to deactivation of the catalyst. Reoxidation by air may regenerate the deactivated catalyst effectively. In comparison with the Mo/HZSM-5 catalyst, the promoted W/HZSM-5-based catalyst can operate under reaction temperature of 1073 K, and gain a methane conversion approximately two times as high as that of the Mo/HZSM-5 catalyst operating at 973 K. It can also operate at 973 K and have about the same methane conversion as that of the Mo/HZSM-5 catalyst at the same reaction temperature. Its main advantage is its heat-resistant performance; the high reaction temperature did not lead to loss of W component by sublimation.

KEY WORDS: methane; dehydro-aromatization; W–Zn (or Mn, La, Zr)/HZSM-5; deactivation and regeneration of W-based catalysts

1. Introduction

Direct catalytic dehydrogenation and aromatization of methane to aromatics (DHAM) such as benzene, toluene, and naphthalene, in the absence of gas-phase oxygen has drawn increasing attention with the development of a series of new catalysts. In the last few years, DHAM reactions over Mo/HZSM-5 [1,2], MoO_3/ZSM-5 and MoO_3/SiO_2 [3], Mo_2C/ZSM-5 [4], Mo–W/HZSM-5 [5], Pt–Mo/HZSM-5 [6], Mo–$ZnSO_4$/HZSM-5 [7], Mo–Ru/HZSM-5 [8] and Mo–Co (or –Fe)/HZSM-5 [9], have been widely developed and studied. However, most of the existing DHAM catalysts, mainly Mo/HZSM-5-based catalysts, operated at about 973 K, which results in rather low methane conversion (X_{CH_4}) due to the thermodynamic limitation. Thermodynamic calculations showed that the equilibrium conversions of 11.3, 15.8, 21, 27 and 33% for methane to benzene (i.e., $6CH_4 \rightleftharpoons C_6H_6 + 9H_2$) are predicted at 973, 1023, 1073, 1123 and 1173 K, respectively. This indicates that an operation temperature as high as $\sim$1073 K is required for methane conversion to reach $\sim$20%. However, under such high temperature, Mo-based catalysts suffer inevitably from the disadvantage of serious loss of Mo component by sublimation. Therefore, development of DHAM catalysts with high activity and stability at higher operation temperatures has potential significance for the commercial utilization of DHAM process.

We have previously reported the development of highly active and heat-resisting W/HZSM-5-based catalysts [10]. Incorporation of Zn (or La) into the W/HZSM-5 catalyst was found to markedly improve the DHAM activity and stability of the catalyst operating under higher temperatures. However, the selectivity data of benzene and toluene products reported previously were obviously higher than realities due to ignoring the portion of methane converted to coke and naphthalene in the selectivity calculations upon the carbon number basis. In the present work, the catalytic tests were conducted with a feed-gas mixture of 90% CH_4 and 10% Ar as internal standard gas. By using an internal standard analyzing method, conversion of methane and selectivities of hydrocarbon products were calculated based on the mass balance of carbon. Effects of reaction conditions on the activity and selectivities of the catalysts were investigated. The results showed that the W/HZSM-5-based catalysts were suitable for operating under reaction temperatures as high as 1073 K to obtain much higher methane conversion and yields of aromatic hydrocarbon without loss of W component. Serious deposition of carbon on the catalyst was found to be the main reason leading to catalyst deactivation. However, the catalyst activity could be recovered by regeneration by air at 823–873 K. It has also been found experimentally that the performance of the W/HZSM-5-based catalysts could be improved by adding some metallic ion such

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as Zn^{2+}, Mn^{2+}, La^{3+} or Zr^{4+}. The results of the present work shed light on the design and development of the practical W/HZSM-5-based catalysts for DHAM reaction.

2. Experimental

The catalysts were prepared by the conventional incipient wetness method, with the HZSM-5 zeolite having a Si/Al molar ratio of 38 (obtained from the Chemical Plant of Nankai Univ., PR China) as carrier. The W/HZSM-5 catalyst was prepared by impregnating a certain amount of the HZSM-5 zeolite carrier with ammonium tungstate aqueous solution containing a calculated amount of W, which was prepared by dissolving $(NH_4)_2WO_4$ (of A.R. grade) in deionized water and adding a small amount of H_2SO_4 to regulate the pH value of the solution to 2–3, followed by drying at 393 K for 2 h, and then calcining at 773 K for 4 h. The Zn (or Mn, La, Zr)-promoted catalyst, W–Zn (or Mn, La, Zr)/HZSM-5, was prepared by firstly impregnating a certain amount of the HZSM-5 zeolite carrier with a calculated amount of $ZnSO_4$ or $MnSO_4$, $La(NO_3)_3$, $ZrOCl_2$ (all of A.R. grade) in aqueous solutions, followed by drying at 393 K for 2 h, and then impregnating with a solution of NH_4OH, drying again at 393 K for 2 h and calcining at 673 K for 4 h, and subsequently impregnating with a calculated amount of H_2SO_4-acidified $(NH_4)_2WO_4$ aqueous solution (pH $=$ 2–3), and finally drying at 393 K for 2 h and calcining at 773 K in air for 5 h. All the catalyst samples were pressed, crushed and sieved to a size of 40–60 mesh.

The activity evaluation of the catalysts for the DHAM reaction was carried out at atmospheric pressure in a continuous flow tubular reactor–GC combination system. A tubular reactor was constructed by quartz tube (8 mm i.d.), and 0.5 g of catalyst sample was used for each test. DHAM reaction over the catalysts was conducted at a stationary state and certain temperatures in the region of 973–1173 K. Prior to DHAM reaction, the catalyst sample was flushed with N_2 at 973 K for 20 min, followed by increasing the temperature to reaction temperature and switching to a feed-gas mixture of CH_4 (of 99.99% purity) with 10% Ar (served as internal standard for GC analysis, of 99.99% purity) at feed-gas hourly space velocity (GHSV) of 960 h^{-1}. The reactant, CH_4, and some small molecule carbon-containing products such as C_2H_6, C_2H_4 and CO, were alternatively determined by an on-line GC (model 103) equipped with dual thermal conductivity detectors (TCD) with a 5A zeolite molecular sieve column and a GDX-502 column separately, and aromatic hydrocarbon products were analyzed by another on-line GC (model 102GD) equipped with a thermal conductivity detector (TCD) and 2 m long dinonyl-phthalate (DNP) column, both with hydrogen as carrier gas. The data were all taken 60 min after the reaction started, unless otherwise specified. With an internal standard analyzing method, X_{CH_4} and selectivities of hydrocarbon products were evaluated. The amounts of coke formed on the catalyst were determined by the TG-DTA method. In most cases, the results of calculation for carbon equilibrium may reach approximately 85% after 1 h of reaction. XPS measurements of the catalysts were carried on a VG ESCA LAB MK-2 system with Mg Kα radiation (10 kV, 20 mA, $h\nu = 1253.6$ eV) under UHV (1×10^{-7} Pa), calibrated internally by the carbon deposit C(1s) (BE) at 284.6 eV. X-ray diffraction measurements were carried out on a Rigaku D/Max-C X-ray diffractometer with Cu Kα radiation at a scanning rate of 8°/min. BET surface area of the catalyst was measured by N_2 adsorption using a Sorptomatic-1900 (Carlo-Erba) system. Ammonia temperature-programmed desorption (NH_3-TPD) test was carried out on conventional temperature-programmed experimental equipment with an Omnistar GSD 3000 MS analyzer.

3. Results and discussion

3.1. Activity of W/HZSM-5 catalyst for DHAM

Figure 1 shows the changes of methane conversion (X_{CH_4}) and selectivity (S_{product}) of several carbon-containing products with increasing temperature from 973 to 1173 K over the 3% (mass percentage) W/HZSM-5 catalyst. The results showed that X_{CH_4} increased with increasing temperature, and reached *ca.* 20% at 1073 K. However, high reaction temperature tends to be favorable for pyrolyzing CH_4 to carbon and some secondary reactions, resulting in a decrease of selectivity to benzene. It can been seen that selectivity to benzene ($S_{C_6H_6}$) reached 60% at 1073 K and descended to 51% at 1173 K. The results of blank experiments shown in table 1 indicated the pyrolysis of methane *via* gas-phase and non-catalytic reactions at 1073 K was limited to a fairly small extent. It seems that 1073 K is an appropriate reaction temperature of DHAM. The experimental result also showed that high temperature was a requisite for reduction activation of the catalyst precursor. Once the catalyst gets activated, it can also operate at temperature as low as 973 K and display certain DHAM activity. Such results are shown in figure 2.

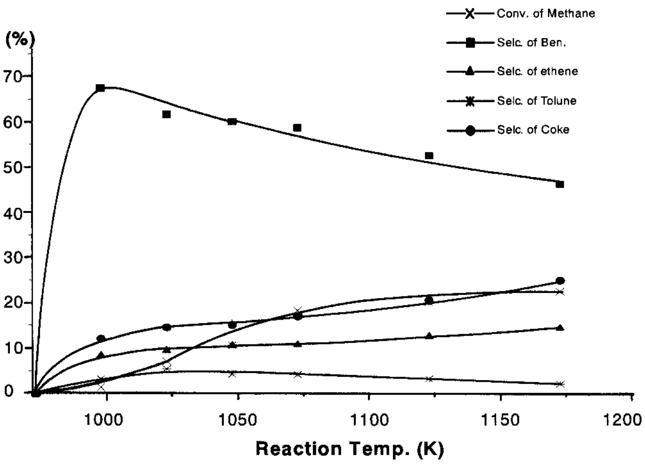

Figure 1. CH_4 conversion and product selectivities over the 3% W/HZSM-5 catalyst for DHAM reaction at different reaction temperatures. Reaction conditions: 0.1 MPa, GHSV of feed-gas CH_4 + 10% Ar at 960 h^{-1}.

Table 1
Results of blank experiments for DHAM reaction.[a]

Catalyst-bed	Temp.	Conv. of CH_4	Selectivity (%)		
material	(K)	(%)	C_2H_4	Benzene	C-deposit
Empty tube	973	–	–	–	–
	1073	0.2	14.3	–	85.7
Quartz chips	973	0.24	9.2	–	90.8
	1073	0.93	3.5	–	96.5

[a] Reaction conditions: 0.1 MPa, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}.

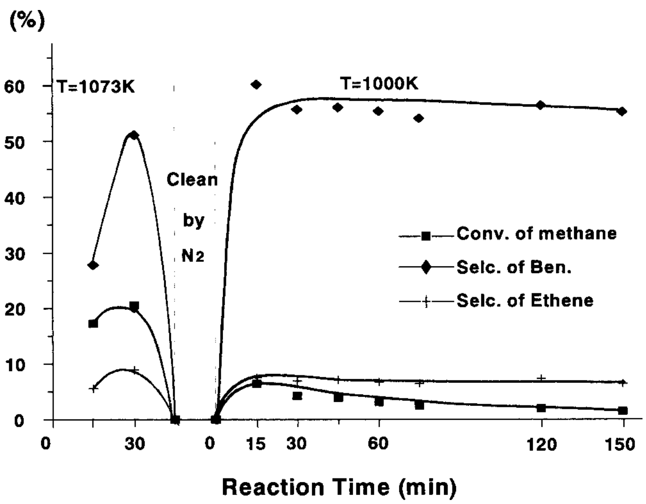

Figure 2. DHAM reaction activity at 1000 K over the 3% W/HZSM-5 catalyst after undergoing a reduction activation at 1073 K. Reaction conditions: 0.1 MPa, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}.

After the reduction activation and reaction in the stream of $CH_4 + 10\%$ Ar feed-gas at GHSV $= 960\ h^{-1}$ at 1073 K for 30 min, followed by flushing the catalyst bed by a stream of nitrogen till there was no product detected in the exit-gas and then lowering the temperature down to 1000 K and subsequently switching to the stream of $CH_4 + 10\%$ Ar feed-gas, the catalyst still displayed a considerable DHAM activity. Under reaction conditions of 0.1 MPa, 1000 K and GHSV of $CH_4 + 10\%$ Ar at 960 h^{-1}, 6–2% conversion of methane and ~56% selectivity of benzene were reached during the following 2 h of reaction.

3.2. Effect of Zn (or Mn, La, Zr) additive on the DHAM activity of the W/HZSM-5 catalyst

It is experimentally found that addition of a small amount of Zn (or Mn, La, Zr) to the W/HZSM-5 catalyst can improve the performance of the catalyst for DHAM reaction to some extent. The results of activity assay of the catalyst systems with different additives for DHAM reaction are listed in table 2.

Changes of methane conversion and selectivities to hydrocarbon products (mainly benzene and naphthalene) with time on stream of the reaction over a 3% W–1.36% Zn/HZSM-5 catalyst were measured under the reaction conditions of 0.1 MPa, 1073 K, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}. The results (see figure 3) showed that after a 20 min inductive period, the methane conversion reached a value of 24–18% in the initial 2 h of reaction, and the corresponding selectivity to benzene, naphthalene, ethylene and coke was 55–50, ~18, ~4 and ~22%, respectively, and the selectivities to ethane and C_7- and C_8-aromatic hydrocarbons below 1% each. After 6 h reaction, the selectivity to coke increased to 35% (with a total amount of coke for the 6 h reaching 16.3 wt% of the catalyst used), while X_{CH_4} and $S_{C_6H_6}$ decreased to ~8 and ~10%, respectively, whereas $S_{C_2H_4}$ increased to 14%. After 12 h reaction, X_{CH_4} dropped to ~2%, and $S_{C_6H_6}$ decreased towards zero, while $S_{C_2H_4}$ came down to 5%. Meanwhile, $S_{C_2H_6}$ went up to 3.2%, with coke as the major carbon-containing product.

Table 2
DHAM reaction activity over the catalyst systems with different additives.[a]

Catalyst	Conv. of CH_4	Selectivity			
	(%)[b]	Ben.	C_2H_4	C_2H_6	Tol.
3% W/HZSM-5	21.8	51.1	6.3	1.7	4.1
3% W/HZSM-5[c]	18.2	48.6	7.8	2.1	3.1
3% W–1.5% Zn/HZSM-5	23.7	53.8	6.1	2.1	4.3
3% W–1.5% Mn/HZSM-5	22.8	55.4	7.2	2.5	4.1
3% W–1.0% La/HZSM-5	22.1	52.6	6.8	1.9	3.2
3% W–1.0% Zr/HZSM-5	23.1	51.9	8.1	2.0	3.6

[a] Reaction conditions: 0.1 MPa, 1073 K, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}.

[b] The best activity data of each catalyst.

[c] Prepared by impregnating the HZSM-5 carrier with the aqueous solution of ammonium tungstate at pH = 7–9 with a desired amount of W, followed by drying at 393 K for 2 h and calcining at 773 K for 4 h.

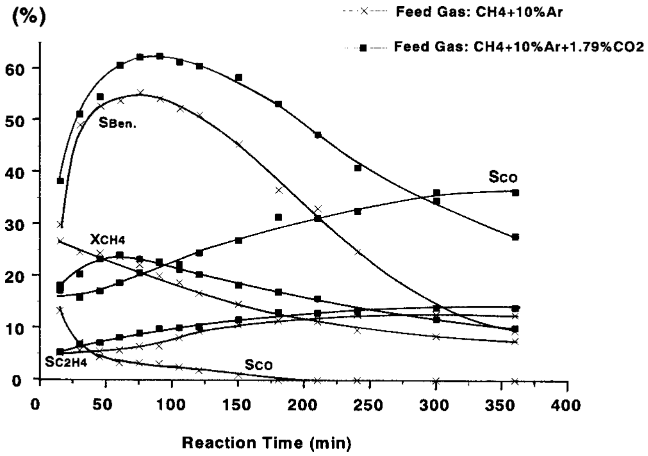

Figure 3. Comparison between the assay results of DHAM reaction activity over the 3% W–1.36% Zn/HZSM-5 catalyst at 0.1 MPa, 1073 K, feed-gas: $CH_4 + 10\%$ Ar *vs.* $CH_4 + 10\%$ Ar $+ 1.8\%$ CO_2, both GHSV $= 960\ h^{-1}$.

3.3. Effects of GHSV and composition of feed-gas on the catalyst activity

The results of the effect of feed-gas GHSV on the catalyst activity are shown in figure 4. With the GHSV increasing from 960 to 3000 h^{-1}, methane conversion and selectivities to benzene and toluene all decreased to a great extent, accompanied by a small increase in selectivities to ethane and ethylene, indicating that high GHSV is unfavorable to methane conversion and formation of aromatic hydrocarbons. This implies that C_2 hydrocarbons are first formed and aromatic hydrocarbons are the products of further conversion of the C_2 hydrocarbons, similar to the case over the Mo/HZSM-5 catalyst [1,2]. In the present work, the GHSV of feed-gas was set at 960 h^{-1}.

Addition of a minor amount of CO_2 to the feed-gas was found to significantly enhance methane conversion and selectivity to benzene and to improve the performance of coke-resistance of W/HZSM-5-based catalysts. Such assay results on the 3% W–1.36% Zn/HZSM-5 catalyst under reaction conditions of 0.1 MPa, 1073 K, GHSV of feed-gas CH_4 + 10% Ar + 1.8% CO_2 at 960 h^{-1} are also shown in figure 3. In the initial 2 h of reaction, ~22% conversion of methane and ~62% selectivity to benzene were reached, and after 6 h of reaction, methane conversion still maintained at ~10%, with the corresponding benzene selectivity at ~38%. The lifetime of the catalyst was thus prolonged to a great extent. The promoting effect of the added CO_2 originated most probably from the role that it played as scavenger of functioning surface of the catalyst *via* the Boudart reaction, $CO_2 + \underline{C}$ (deposited C at surface) → 2CO, thus in favor of alleviating the deposition of carbon and inhibiting the formation of coke at the catalyst surface to a greater extent. This is analogous to the cases of DHAM reaction over the Mo/HZSM-5-based catalysts with 4% $CO_2 + CH_4$ as feed-gas and the preparation reaction of bulk tungsten carbide catalysts reported by [9,11], respectively.

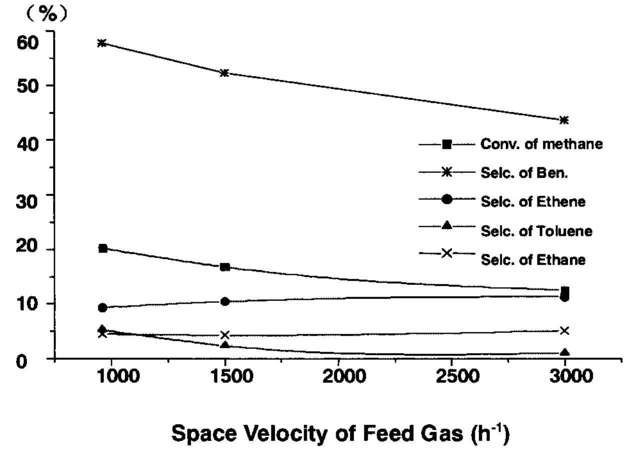

Figure 4. Effect of feed-gas GHSV on the activity of the 3% W/HZSM-5 catalyst. Reaction conditions: 0.1 MPa, 1073 K, feed-gas composition CH_4 + 10% Ar.

The experimental result indicated that the amount for addition of CO_2 in the feed-gas should be less than 2%. When the adding amount of CO_2 was more than 2%, it would be difficult to start up the reaction. This implied that the catalytically active sites/phase of W/HZSM-5-based catalysts were easier to be oxidized in comparison with those of Mo/HZSM-5-based catalysts. In the case of Co- and Fe-modified Mo/HZSM-5 [9], the amount of CO_2 in the feed-gas can be as high as 4%, or even much higher.

3.4. *Deposition of carbon on the catalyst and deactivation and regeneration of the catalyst*

By means of XPS measurements, the molar ratios of the component elements at the XPS-detectable surface layer of several catalyst samples can be estimated and they are listed in table 3. It can be seen that the molar ratio of the component elements at the surface of the 3% W/HZSM-5 catalyst was Al/C/O/Si/W = 1.2/~0/63.1/34.4/1.3 for the oxidation precursor of the catalyst, and 1.5/41.7/35.5/20.8/0.5 for the functioning catalyst after 1 h reaction. It changed to Al/C/O/Si/W = 0.6/82.7/10/6.6/0.1 after 6 h reaction, revealing that most of the surface of the functioning catalyst was covered by carbon deposits. NH_3-TPD measurements showed that *ca.* 80% of strong and medium-strong acidic sites (with those of the oxidation precursor of catalyst as 100%) were lost after 5 h of reaction (see figure 5). N_2-BET measurements demonstrated that, after 1 h reaction, the specific surface area of the functioning catalyst decreased to 302 from 368 $m^2\ g^{-1}$ for the oxidation precursor of catalyst. It further came down to 75 $m^2\ g^{-1}$ after 5 h of reaction (also see figure 5), implying that most of the zeolite pores were

Table 3
Molar ratios of the component elements at the XPS-detectable surface layer of several catalyst samples.

Catalyst sample	State	Element composition (mol%)					
		Al	C	O	Si	W	Zn
3% W/HZSM-5	Oxidation precursor	1.2	~0	63.1	34.4	1.3	–
	After 1 h of reaction	1.5	41.7	35.5	20.8	0.5	–
	After 3 h of reaction	0.7	75.0	14.3	9.7	0.3	–
	After 6 h of reaction	0.6	82.7	10.0	6.6	0.1	–
	After 6 h of reaction followed by reoxidation	1.8	~0	64.7	31.7	1.9	–
3% W–1.5Zn/HZSM-5	Oxidation precursor	2.1	~0	64.6	31.8	1.1	0.4
	After 1 h of reaction	1.6	39.1	37.6	21.0	0.5	0.2
	After 3 h of reaction	0.7	66.8	20.0	12.0	0.4	0.1
	After 6 h of reaction	0.6	78.3	12.6	8.2	0.2	0.1
	After 6 h of reaction followed by reoxidation	2.4	~0	65.8	29.7	1.6	0.5

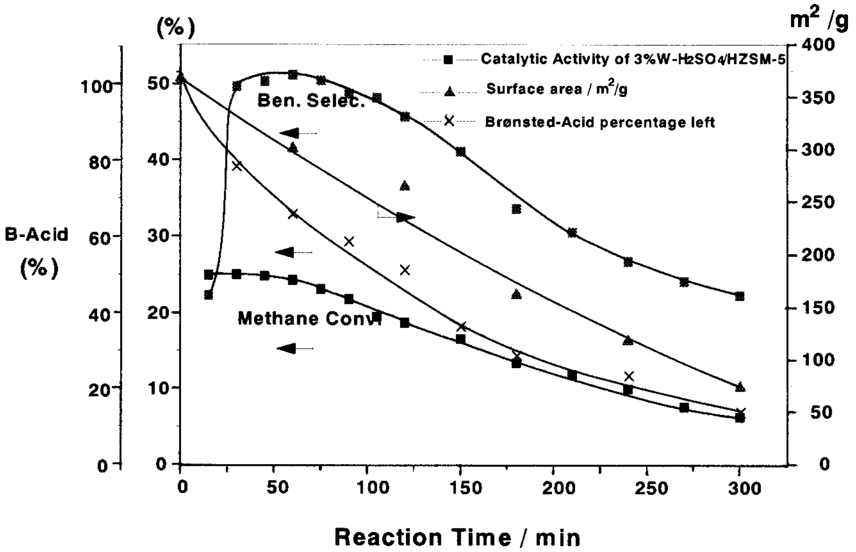

Figure 5. Changes of activity and surface B-acid percentage as well as specific surface area of the functioning 3% W/HZSM-5 catalyst with time on stream of the reaction at 1073 K.

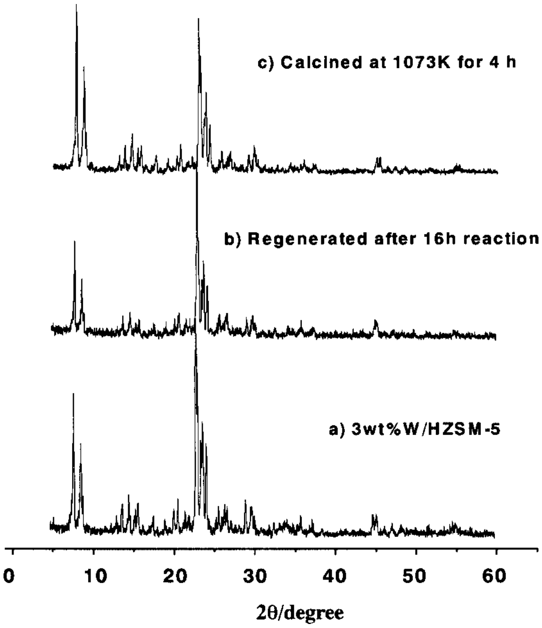

Figure 6. XRD patterns of: (a) the as-prepared 3% W/HZSM-5 precursor, (b) the 3% W/HZSM-5 catalyst used for DHAM operation for 16 h and then regenerated by air oxidation at 873 K for 1 h and (c) the 3% W/HZSM-5 precursor calcined at 1073 K for 4 h.

blocked by carbon deposits at that time, thus resulting in the loss of a greater part of the surface. In fact, heavy deposition of carbon on the surface of the functioning catalyst was the main reason leading to deactivation of the catalyst.

Reoxidation by air can regenerate the deactivated 3% W/HZSM-5 catalyst effectively, with the Al/C/O/Si/W molar ratio at the renewed surface recovered to 1.8/~0/64.7/31.7/1.9 (see table 3) and the X_{CH_4} and $S_{\mathrm{C}_6\mathrm{H}_6}$ regained to 20–18 and *ca.* 50%, respectively, after undergoing an induction period of 20 min. XRD measurements showed that there was no distinct difference between XRD features of the 3% W/HZSM-5 catalyst used for DHAM operation for 16 h and then regenerated by air-oxidation at 873 K for 1 h and that of the corresponding catalyst precursor as-prepared or calcined at 1073 K for 4 h (see figure 6). This indicates that there is little significant damage in the phase structure of the catalyst occurring after undergoing the cycle of DHAM operation/air regeneration. Figure 7 shows the results of activity evaluation of the 3% W–1.5% Mn/HZSM-5 catalyst for DHAM reaction after a series of operation/regeneration (by air oxidation each time for 1 h at 873 K). It is not until after ten times of regeneration that a small decrease in the catalyst activity was observed. It seems that the reason leading to the decrease in the catalyst activity was probably due to dealuminization to some degree of the framework structure of HZSM-5 zeolite caused by aqueous vapor resulting from the coke combustion in air regeneration processes over and over again.

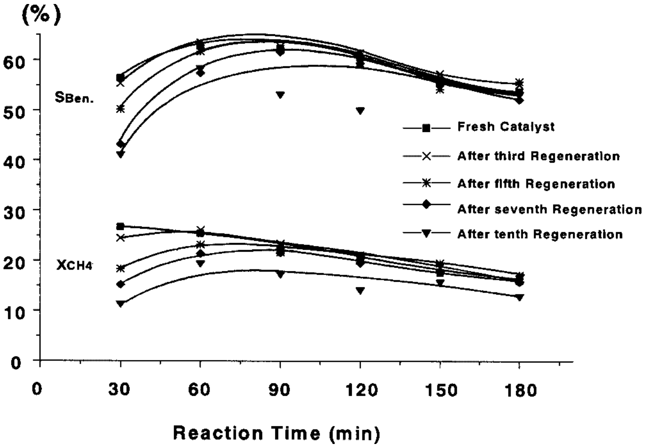

Figure 7. DHAM reaction activity over the 3% W–1.5% Mn/HZSM-5 catalyst after undergoing a series of operation/air regeneration. Reaction conditions: 0.1 MPa, 1073 K, GHSV of feed-gas $\mathrm{CH}_4 + 10\%$ Ar at 960 h^{-1}; the below curves for methane conversion and the upper curves for benzene selectivity.

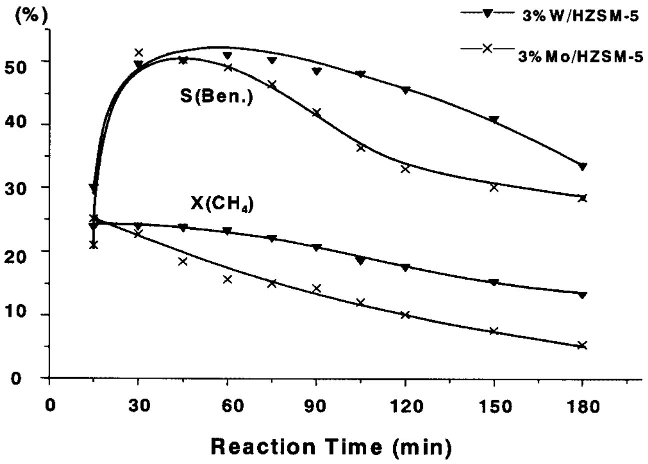

Figure 8. Comparison between W/HZSM-5 and Mo/HZSM-5 catalysts in their activity for DHAM. Reaction conditions: 0.1 MPa, 1073 K, GHSV of feed-gas CH_4 + 10% Ar at 960 h^{-1}.

3.5. Comparison of the W/HZSM-5-based catalysts with the Mo/HZSM-5-based catalysts

High reaction temperature is evidently beneficial to enhancing methane conversion; however, as the reaction proceeds, it inevitably makes coking more seriously, eventually leading to deactivation of the catalyst. The same situations happened to both the W/HZSM-5-based and the Mo/HZSM-5-based catalysts. One of the main differences between W/HZSM-5 and Mo/HZSM-5 catalysts is in their stabilities under high temperature. As shown in figure 8, both of them did have high initial activity for DHAM reaction at 1073 K. However, the activity of Mo/HZSM-5 catalyst began to decrease after 1 h reaction, accompanied by the appearance of a pale-yellow deposit, likely resulting from sublimation of the Mo component, on the inner wall of the exit tube of the reactor. The W/HZSM-5-based catalyst can operate under reaction temperature of 1073 K and gain a methane conversion approximately two times as high as that of the Mo/HZSM-5 catalyst operating at 973 K. It can also operate at 973 K and have about the same methane conversion as that of the Mo/HZSM-5 catalyst at the same reaction temperature. Its main advantage is its heat-resistant performance. The high reaction temperature did not lead to loss of W component by sublimation. Thus, it could withstand the regeneration operation by air to a greater extent. By incorporating proper additives, the concentration and intensity of the surface acid sites could be refined and controlled, the reducibility of the catalyst could be improved, and the coking and deposition of carbon at the functioning surface of the catalyst could be reduced to a greater extent. Works in these aspects will be reported in a follow-up article.

4. Conclusions

(1) With incorporation of Zn (or Mn, La, Zr) into the W/HZSM-5 catalyst, highly active and heat-resisting W/HZSM-5-based catalysts for DHAM reaction have been developed. The W–Zn (or Mn, La, Zr)/HZSM-5 catalyst can operate under a reaction temperature of 1073 K and gain a methane conversion approximately two times as high as that of Mo/HZSM-5 operating at 973 K. It may also operate at 973 K and have about the same methane conversion as that over the Mo/HZSM-5 catalyst operating at the same temperature. The high operation temperature did not lead to the loss of W component by sublimation.

(2) Addition of a small amount of CO_2 ($\leqslant$2%) to the feed-gas was found to significantly enhance methane conversion and selectivity of benzene, and to improve the performance of coke resistance of the W/HZSM-5-based catalysts.

(3) Heavy deposition of carbon on the surface of the functioning catalyst was the main reason leading to deactivation of the catalyst. By means of re-oxidation by air at 873 K, the deactivated catalyst could be effectively regenerated.

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