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## Abstract

The catalytic conversion of CH<sub>3</sub>Br to aromatics was investigated over PbO-modified HZSM-5. The effects of PbO loading, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5, and calcination conditions of catalyst on catalytic performance were studied. It was found that the most suitable PbO loading and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is 5 wt% and 70, respectively, and the 5wt%PbO/HZSM-5 calcined at 450°C for 8 h performs the best. Also, PbO is superior to the other metal oxides selected to modify HZSM-5, and

HZSM-5 is better than SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> as support. The characterization results indicate that (i) the PbO species is highly dispersed on the HZSM-5 support, (ii) the role of PbO is to promote hydrocarbon aromatization, and (iii) the acid sites of HZSM-5 are indispensable for CH<sub>3</sub>Br conversion into aromatics. We found that the deactivation of catalyst is due to pore blocking by carbonaceous deposits. The overall results demonstrate that the method is efficient for the conversion of CH<sub>4</sub> to aromatics.

**Keywords:** Bromomethane; Aromatics; HZSM-5; lead oxide

## 1. Introduction

In view of the declining resources and high price of crude oil, the conversion of natural gas has attracted much attention in the past three decades <sup>[1]</sup>. Aromatic compounds such as benzene, toluene, xylene, trimethylbenzene are important raw materials of industrial processes. It is hence desirable to transform natural gas into aromatics that are currently produced from petroleum, and significant progresses have already been made. Wang et al. <sup>[2]</sup> reported that methane, the major component of natural gas, could be directly converted to aromatics in the absence of oxygen over modified HZSM-5 catalysts. At 700°C and  $GHSV_{\text{methane}}=1500 \text{ ml}/(\text{g}\cdot\text{h})$ , methane conversion was 7-10% and aromatic selectivity 80-90%, but deactivation of catalysts due to coke formation remains a major problem. Another process is the synthesis gas (syngas) route that includes the sequential steps of (i) syngas production from methane, (ii) methanol generation from syngas, and (iii) aromatics formation from methanol <sup>[3-10]</sup>. The yield of aromatics through the syngas route, however, is not satisfactory.

In the past decade, efforts have been made to develop new processes such as that using  $\text{Cl}_2$  or  $\text{Br}_2$  as mediator for methane activation <sup>[11-16]</sup>. The process is generally considered stoichiometric rather than catalytic. However, due to the high reactivity of  $\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  which are difficult to convert to higher hydrocarbons are usually formed <sup>[12,16]</sup>. Another process for the conversion of methane to higher hydrocarbons involves the use of “ $\text{HCl} + \text{O}_2$ ” as agent for methane activation <sup>[17-19]</sup>. It is noted that the yields of aromatics in the processes are low, and

the approach cannot be used for aromatics production from methane. Recently, a route has been developed for the catalytic conversion of methane using HBr as mediator in the presence of oxygen and H<sub>2</sub>O [20-26]. The method involves the conversion of methane into CH<sub>3</sub>Br over a suitable catalyst, followed by the catalytic transformation of CH<sub>3</sub>Br to higher hydrocarbons and/or other compounds. The steps are conducted at atmospheric pressure and the bromine element is recycled and reused. It was pointed out that HBr is a chemical safer to handle than Br<sub>2</sub>, and the use of water enables the timely removal of heat generated in the exothermic reaction. Different from the use of Cl<sub>2</sub> or HCl+O<sub>2</sub>, the use of HBr results in high selectivity to monohalomethane. Also, since C-Br bond is weaker than C-Cl bond, CH<sub>3</sub>Br is a better intermediate than CH<sub>3</sub>Cl for the formation of hydrocarbons of higher carbon numbers.

Previously, liquid fuels such as methanol and C5 hydrocarbons are the target products in the studies of methane activation and CH<sub>3</sub>Br conversion [27-32]. It is apparent that the bromination of CH<sub>4</sub> using Br<sub>2</sub> or HBr+O<sub>2</sub> as mediator is a feasible route. The one-through conversion of methane over Rh/SiO<sub>2</sub> at 660°C is 30-36%, and CH<sub>3</sub>Br selectivity is in the range of 79%-83% [28, 29]. We have done a comprehensive literature search and found that there is no report on the conversion of CH<sub>3</sub>Br into aromatic chemicals. We have also made an economic assessment of the process and the outcome shows that the approach is more attractive than the traditional one using petroleum as raw material. We hence conducted systematic research on the topic using HZSM-5 and modified HZSM-5 as catalysts, and investigated the effects of composition and preparation conditions of the catalysts on catalytic performance. We

also looked into factors such as reaction mechanism, catalyst deactivation, and catalyst regeneration.

## **2. Experimental**

### *2.1 Chemicals and reagents*

Most of the reagents and chemicals (analytic grade) were purchased from Changsha Huihong Chemical Co. The HZSM-5 molecular sieves were from Shanghai Fuxu Molecular Sieve Co and aqueous HBr (HBr concentration  $\geq 40\text{wt}\%$ ) was from Tianjin Damao Chemical Reagent Co. The gases 5%-CO<sub>2</sub>/He, 5%-NH<sub>3</sub>/He, He (99.999% purity), and N<sub>2</sub> (99.999% purity) were bought from Changsha Gas Co. All the chemicals and reagents were used without further purification or treatment.

### *2.2 Catalyst preparation*

The catalysts of modified HZSM-5 were prepared by wetness incipient impregnation with water as solvent, followed by drying at 110°C for 12 h and calcination in a muffle furnace. The reagents used as precursors for HZSM-5 modification were La(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 50wt%Mn(NO<sub>3</sub>)<sub>4</sub> solution, (NH<sub>4</sub>)<sub>6</sub>W<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, and NH<sub>4</sub>VO<sub>3</sub> (analytic grade). Unless otherwise specified, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5 was 70, loading of metal oxide (MO) in a catalyst was 5wt%, and calcination of catalysts was conducted at 450°C for 8 h.

### *2.3 Catalyst characterization*

The actual loading of MO in the prepared catalysts was determined over a sequence XRF-1700 X-ray fluorescent spectrometer (Shimadzu) at a setting of 40 kV and 95 mV. We found that the actual MO loading of PbO/HZSM-5 and MoO<sub>3</sub>/HZSM-5 was similar to the nominal value (5 wt%). The BET surface area, pore volume and pore size of supports and catalysts were measured using a Micromeritics 2010C instrument; before each measurement, the sample was heated to 300°C and kept at this temperature for 5 h. Powder X-ray diffraction experiment was conducted on a Rigaku Automatic Diffractometer (Rigaku D-MAX) with monochromatized Cu K<sub>α</sub> radiation ( $\lambda=0.15406$  nm) at a setting of 40 kV and 80 mA. The recorded patterns were referred to the powder diffraction files-1998 ICDD PDF Database for phase identification. TEM was used to investigate the morphology and particle size of catalysts; images were taken on a JEM-2010F transmission electron microscope operating at 200 kV. TG and DSC studies were performed over a STA449C instrument (Netzsch) in the temperature range of 20-800°C in air (flow rate 50 ml/min), with heating rate = 10°C/min and initial sample weight = 10 mg.

NH<sub>3</sub>- or CO<sub>2</sub>-TPD experiments of catalysts were conducted on a Micromeritics 2920 apparatus using thermal conductivity detector (TCD). Before measurement, the sample (0.2 g for all catalysts) was treated at 360°C for 1 h and cooled to 100°C in helium flow. Then the gas flow was switched to 5%-NH<sub>3</sub>/He (or 5%-CO<sub>2</sub>/He) for 30 min for adsorption of NH<sub>3</sub> (or CO<sub>2</sub>). After adsorption, the gas flow was switched to pure He (60 ml/min). NH<sub>3</sub>-TPD (or CO<sub>2</sub>-TPD) was performed (heating rate =

15°C/min) once a stable baseline was established (after around 40 min in a flow of He at room temperature). The desorbed amount was estimated by calibration of peak area against the TCD signal of a known amount of NH<sub>3</sub> (or CO<sub>2</sub>).

X-ray photoelectron spectroscopic (XPS) measurements were carried out on a Leybold Heraeus-Shengyang SKL-12 electron spectrometer with a VG CLAM 4 MCD electron energy analyzer. Mg-K<sub>α</sub> X-ray radiation ( $h\nu = 1253.6$  eV) was generated at 15 mA and 10 kV. Peaks of Si<sub>2p</sub>, Al<sub>2p</sub>, C<sub>1s</sub>, O<sub>1s</sub>, Si<sub>2s</sub> and Pb<sub>4f</sub> were recorded in binding energy interval of 0.1 eV. The energy scale was corrected by using the binding energy of zeolitic Si<sub>2p</sub> at 103.0 eV as internal standard. The spectrometer chamber had a residual gas pressure close to  $2 \times 10^{-7}$  Pa during data acquisition.

#### *2.4 Catalytic evaluation*

The evaluation of catalysts was conducted over a continuous fixed-bed quartz reactor (Scheme 1). The CH<sub>3</sub>Br was prepared from CH<sub>3</sub>OH and HBr in the first reactor that was filled with HZSM-5. We observed complete conversion of CH<sub>3</sub>OH and 100% selectivity to CH<sub>3</sub>Br. To remove HBr and water, the gas effluent from the first reactor was passed through aqueous NaOH solution and MgSO<sub>4</sub> particles before being directed into the second reactor that was filled with HZSM-5 or a MO-modified HZSM-5 catalyst. The aromatization of CH<sub>3</sub>Br was conducted at 360°C with  $WHSV_{CH_3Br}$  (grams of reactant fed per gram catalyst per hour) = 1.34 h<sup>-1</sup> (or 0.67 h<sup>-1</sup>) and N<sub>2</sub> flow rate = 5 ml/min.

In general, the reaction was unstable within the first 1.5 h and the initial products were removed and not analyzed. After this period, the effluent was cooled by means of an ice-water bath for the collection of liquid products. The gaseous as well as the liquid products were qualitatively analyzed at different time intervals on a GC/MS (6890N/5973N) using an Agilent HP-5MS capillary column (30m×0.45mm×0.8μm). For quantitative determination, the gaseous products were analyzed on an Agilent 6890N GC with TCD and Agilent GS-GASPRO capillary column (30m×0.32mm×0.25μm), whereas the liquid products on an Agilent 6820N GC with TCD and Agilent DB-WAX capillary column (30m×0.45mm×0.8μm). The CH<sub>3</sub>Br conversion, aromatic yield and product distribution results were based on the averaged values of the data collected at different time intervals within a period of 4 h.

[Scheme 1]

### **3. Results and discussion**

#### *3.1 Catalytic results*

##### *3.1.1 Effect of modifier*

In order to identify a good modifier, we conducted systematic investigation on a series of MO. The loading of MO on HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=70) was 5wt%. As depicted in Table 1, the MO-modified HZSM-5 catalysts show CH<sub>3</sub>Br conversion better than that of HZSM-5. In terms of aromatics yield, Bi<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, and PbO are good promoters, with promotion effects (as compared to the aromatic yield of HZSM-5 (21.5%)) in the order of Bi<sub>2</sub>O<sub>3</sub> (25.2%) < La<sub>2</sub>O<sub>3</sub> (28.9%) < MoO<sub>3</sub> (30.7%) <

PbO (31.6%). It is clear that the PbO/HZSM-5 catalyst performs better than MoO<sub>3</sub> which is known to be good for methane or methanol aromatization [2,30,31,32]. It is worth pointing out that MgO promotes the formation of low-carbon alkane or olefin rather than the formation of aromatics, plausibly due to its basic nature.

[Table 1]

The product distribution over the MO-modified HZSM-5 catalysts is rather complex. It is found that propane and butane are dominant in the gas phase. On the other hand, aromatics are the major liquid products, and no aliphatic compounds (e.g. pentane, pentene, hexane, heptane, etc.) are detected. Over PbO/HZSM-5, the selectivity to benzene, toluene, xylene, and trimethylbenzene is 0.4%, 3.1%, 18.8%, and 42.4%, respectively. We studied the effect of PbO loading on the catalytic performance of PbO/HZSM-5. As shown in Figure 1, with the rise of PbO loading (from 3 to 10 wt%), CH<sub>3</sub>Br conversion goes through a minimum while aromatic yield a maximum, and the lowest conversion and highest yield appears at PbO loading of ca. 4 and 5 wt%, respectively. It is deduced that the variation of CH<sub>3</sub>Br conversion and aromatic yield versus PbO loading possibly results from the change of surface acidity and pore channels of the catalysts; PbO in excess will result in covering of active sites on HZSM-5 and blockage of HZSM-5 pore channels, thus hampering the promotion effect of PbO.

[Figure 1]

### 3.1.2 Effect of support

Since PbO is the best modifier, we adopted it (5wt%) to examine the effect of using SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> as support rather than HZSM-5 on the aromatization reaction. As shown in Figure 2, CH<sub>3</sub>Br conversion over the PbO-modified catalysts can be ranked in the following order: HZSM-5 (97.8%) >> Al<sub>2</sub>O<sub>3</sub> (20.0%) > ZrO<sub>2</sub> (2.7%) > SiO<sub>2</sub> (1.7%). Moreover, PbO/HZSM-5 shows the highest aromatics yield (30.6%), much higher than that of the others. In the case of PbO-modified SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>, almost no aromatics are generated. The excellent “support effect” of HZSM-5 for CH<sub>3</sub>Br conversion should be similar to that for the transformation of methanol into aromatics [6,8,9,10,32,33]. It is known that the two-dimensional structure of HZSM-5 channels is based on 10-membered rings, and the channels of HZSM-5 are wide enough for the C<sub>2v</sub> isomer of tetramethylbenzene (durene) to diffuse out. Also, the channels of HZSM-5 provide enough space for the cyclization and intermolecular hydride transfer reactions through which olefins can be converted into alkanes and aromatics. Moreover, Trombetta et al. [34] pointed out that the B acid sites of bridging hydroxyl groups (Si-OH-Al) have a significant role to play in the direct aromatization of methane. It is deduced that the microporous structure and acid sites of HZSM-5 are essential for CH<sub>3</sub>Br aromatization.

[Figure 2]

The effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of HZSM-5 molecular sieves on the aromatization reaction was also investigated. For comparison, both pure and modified HZSM-5 was examined. As shown in Figure 3, with rise in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio both CH<sub>3</sub>Br conversion and aromatics yield go through a maximum, and aromatics yield reaches

its highest point at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio = 70.

[Figure 3]

### 3.1.3 Effect of catalyst calcination conditions

In general, the conditions of catalyst calcination have an effect on the performance of supported catalysts. We investigated the effects of calcination temperature and time on the catalytic performance of PbO/HZSM-5. From Figure 4, one can see that  $\text{CH}_3\text{Br}$  conversion increases with the rise of calcination temperature (from 360 to 550°C). On the other hand, aromatics yield comes to a maximum at calcination temperature of 450°C. It is known that lead nitrate decomposes into PbO and  $\text{NO}_2$  at ca. 470°C in air. If the calcination temperature was much lower than 470°C, lead nitrate decomposition would not be complete and the promotion effect of PbO would not be manifested. On the other hand, if the calcination temperature was too high, the PbO particles loaded on HZSM-5 would congregate, resulting in poor dispersion of PbO and even blockage of micropores. At 470°C, we have complete decomposition of lead nitrate and dispersion of the as-generated PbO particles into the HZSM-5 channels.

[Figure 4]

Figure 5 shows the effect of calcination time (2-10 h) on catalytic performance. It is clear that the variation of time has little effect on  $\text{CH}_3\text{Br}$  conversion but maximum aromatic yield of 30.6% was observed at a calcination time of 8 h. Accordingly, we selected calcination temperature = 450°C and calcination time = 8 h for the fabrication of the PbO/HZSM-5 catalyst.

[Figure 5]

### 3.1.4 Effect of reaction conditions

As depicted in Figure 6, CH<sub>3</sub>Br conversion comes to a maximum at 400°C while aromatic yield comes to a maximum at 360°C. Generally speaking, increase of reaction temperature would result in enhancement of reaction rate. The decline in CH<sub>3</sub>Br conversion above 400°C and aromatics yield above 360°C could be related to catalyst deactivation caused by coke formation.

[Figure 6]

Table 2 shows the effect of the space velocity of CH<sub>3</sub>Br on CH<sub>3</sub>Br conversion, aromatic yield, and product distribution over 5wt%PbO/HZSM-5. With  $WHSV_{CH_3Br}$  varied from 0.67 to 5.36 h<sup>-1</sup>, there is significant decline in CH<sub>3</sub>Br conversion and aromatic yield. As listed in Table 2, with increase of space velocity, the contents of alkyl benzenes such as those of C<sub>6</sub> ~ C<sub>9</sub> species in liquid increase, whereas the concentrations of C<sub>10-13</sub> aromatic species decrease. Therefore, it is deduced that alkylation of the benzene is favored at low space velocity.

[Table 2]

### 3.1.5 Catalyst stability and recyclability

Catalyst stability and regeneration of deactivated catalysts were tested over the 5wt%PbO/HZSM-5 catalyst and the results are compared with those of 5wt%MoO<sub>3</sub>/HZSM-5 and HZSM-5. As shown in Figure 7, CH<sub>3</sub>Br conversion over PbO/HZSM-5 declines from ca. 98% to 65% in 41 h, that over HZSM-5 declines from ca. 91% to 65% within 30 h, whereas that over MoO<sub>3</sub>/HZSM-5 declines from ca. 97% to 65% within 15 h. It is obvious that the deactivation rate of PbO/HZSM-5 and

HZSM-5 are rather similar. In terms of catalyst stability, PbO/HZSM-5 is superior to MoO<sub>3</sub>/HZSM-5. In other words, introducing PbO to HZSM-5 enhances activity and selectivity but has no ill effect on catalyst stability.

[Figure 7]

For reactivation of spent catalyst, the used PbO/HZSM-5 catalyst was heated in a flow of 20%O<sub>2</sub>/N<sub>2</sub> at 550°C for 4 h. As shown in Figure 7, the reactivated catalyst performs well and the decline of CH<sub>3</sub>Br conversion and aromatic yield is minimal in a test of 3 cycles. The results show that the catalyst is recyclable and suitable for reuse.

### ***3.2 Catalyst characterization***

In order to disclose the relationship between catalytic performance and catalyst structure, and to find out the cause of catalyst deactivation, techniques such as N<sub>2</sub> physio-adsorption, XRD, TEM, TG, DSC, and TPD were employed to characterize the catalysts.

#### ***3.2.1 N<sub>2</sub> physio-adsorption***

As listed in Table 3, the surface area and pore volume of fresh HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=70) is 359.5 m<sup>2</sup>/g and 0.2023 ml/g, respectively. The loading of 5 wt% PbO on HZSM-5 leads to slight decline in surface area (from 359.5 to 343.7 m<sup>2</sup>/g) as well as in pore volume (from 0.2023 to 0.1910 ml/g). It is hence regarded that the improvement of catalytic activity induced by PbO modification has little to do with the change of catalyst texture. After reaction at 360°C for 5.5 h, the PbO/HZSM-5

catalyst declined significantly in surface area (to 234.5 m<sup>2</sup>/g) and in pore volume (to 0.1412 ml/g). After 41 h, there was further decline of surface area (to 144.69 m<sup>2</sup>/g) and pore volume (to 0.0917 ml/g). It is apparent that catalyst deactivation is mainly due to the blocking of pores by deposited materials.

[Table 3]

### 3.2.2 XRD

The results of XRD investigation of HZSM-5 and fresh and used PbO/HZSM-5 catalysts are shown in Figure 8. We detect the characteristic peaks of HZSM-5 over all the samples (Figure 8, a-e). There are no signals ascribable to PbO over the 5wt%PbO/HZSM-5 or 10wt%PbO/HZSM-5 sample (Figure 8, b & d). Similar results were observed over MoO<sub>3</sub>/HZSM-5 catalysts by Wang et al. [2]. The XRD results suggest that PbO is highly dispersed on HZSM-5. We detect no signals of PbO or PbBr<sub>2</sub> over the used and recycled (4 times) PbO/HZSM-5 catalyst (Figure 8, c, e). It is deduced that the dispersed PbO particles are stable under the adopted reaction conditions. The aggregation of PbO particles or the conversion of PbO into lead bromide should be minimal. However, in the case of MgO/HZSM-5, MgO is converted to MgBr<sub>2</sub> entities that are reckoned as ‘active sites’ for the conversion of halomethane into higher hydrocarbons [35].

[Figure 8]

### 3.2.3 TEM, EDS

The results of TEM investigation provide further information related to the morphology and dispersion of PbO. The particle size of HZSM-5 molecular sieve is in the 0.2-4  $\mu\text{m}$  range (average size: 2  $\mu\text{m}$ ), and the PbO particles are too small to be recognized (Figure 9a). Comparing the image of HZSM-5 (Figure 9b) with that of fresh PbO/HZSM-5 (Figure 9c), the circled black spot in Figure 9c should be due to a PbO particle. The result of EDS analysis on fresh catalyst (Figure 9d) shows elements of PbO and HZSM-5, and the composition (atom%) is C, 10.13; O, 34.39; Al, 1.65; Si, 25.21; Cu, 27.82; Pb 0.79. The results provide another piece of evidence that the PbO particles are highly dispersed on HZSM-5. In addition, the result of EDS analysis on used PbO/HZSM-5 catalyst (Figure 9e) shows that elemental composition (atom%) is: C, 65.83; O, 9.86; Si, 5.78; Cu, 15.59; Br 0.74. The C content of the used catalyst is much higher than that of the fresh catalyst, confirming the deposition of carbonaceous species during  $\text{CH}_3\text{Br}$  aromatization.

[Figure 9]

#### 3.2.4 $\text{NH}_3$ (or $\text{CO}_2$ ) -TPD

The results of  $\text{NH}_3$ -TPD experiments over HZSM-5, 5wt%-PbO/HZSM-5, 5wt%-MgO/HZSM-5 are shown in Figure 10. Generally speaking, for the measurement of acidity of HZSM-5 zeolite, the TPD profiles are deconvoluted into three peaks denoted as  $\alpha$ ,  $\beta$  and  $\gamma$ . The  $\alpha$  peak below  $200^\circ\text{C}$  is related to physisorbed ammonia or ammonia adsorbed on external silanol groups<sup>[36,37]</sup>. The  $\beta$  peak at about  $380^\circ\text{C}$  is assigned to  $\text{NH}_3$  adsorbed on extra-framework aluminum species<sup>[38]</sup>,

whereas the  $\gamma$  peak in the 400 ~ 600°C range is attributable to ammonia strongly adsorbed on the Brønsted acid sites located inside the channels of the zeolite. The corresponding sites are commonly denoted as  $\alpha$ ,  $\beta$  and  $\gamma$  acid sites.

[Figure 10]

The results of surface acidity estimated from the curves of Figure 11 are shown in Table 4. A comparison between the blank HZSM-5 and 5wt%PbO/HZSM-5 samples reveals that the introduction of 5wt%PbO into HZSM-5 zeolite results in a significant decrease of  $\beta$  sites (from 0.498 mmol/g to 0.122 mmol/g) and a slight increase of  $\alpha$  and  $\gamma$  sites. Overall the total amount of surface acid sites decreases, which is partly due to sites of PbO being covered. The NH<sub>3</sub>-TPD profile of 5wt%MgO/HZSM-5 exhibits only one peak at 162°C, a temperature corresponds to weak acid sites; the  $\beta$  and  $\gamma$  peak cannot be found. However, the CO<sub>2</sub>-TPD profile of 5wt%MgO/HZSM-5 (Figure 11) exhibits peaks at 153, 309 and 543°C. The total amount of basic sites is 0.232 mmol/g. In addition, no CO<sub>2</sub>-TPD signals are detected over pure HZSM-5 and 5wt%PbO/HZSM-5. It is hence clear that compared to 5wt%PbO/HZSM-5, MgO/HZSM-5 is more basic in nature.

[Table 4]

[Figure 11]

### 3.2.5 TG and DSC

To find out the cause of catalyst deactivation, we analyzed the used

PbO/HZSM-5 catalysts by TG and DSC techniques. The TG and DSC curve of the catalyst used in 5.5 and 41 h of on-stream reaction are shown in Figure 12(a) and 12(b), respectively. Generally, the weight loss below 100°C is attributed to the desorption of surface water adsorbed during exposure of sample to air, whereas the weight loss in the 350 - 700 °C range to the removal or burning-off of surface deposits. With prolonged reaction time (5.5 to 41 h), the weight loss in the 350 - 700 °C range changed from 7.5 to 9.9 wt %, indicating that the growth of carbonaceous deposition with time-on-stream. The DSC profiles of the 5.5- and 41-h samples show pronounced exothermic events at ca. 250, 437 and 535°C. It is deduced that there are possibly three types of carbonaceous deposition. Of course, one can argue that the discrepancy of temperature could be due to only one type of carbon but on different surfaces such as those inside or outside the channels of HZSM-5.

[Figure 12]

### 3.2.6 XPS

Figure 13 shows the C1s spectra of 5wt%PbO/HZSM-5 catalysts collected after 5.5 and 41 h of reaction. Two kinds of carbon species can be detected. The one with C1s binding energy of  $284.6 \pm 0.1$  eV is ascribable to graphitic carbon. Another kind of carbon species with C1s binding energy of  $287.0 \pm 0.1$  eV is attributed to C-Br species. The results of XPS investigation by Wang et al. <sup>[39]</sup> indicated the presence of three types of carbon on used Mo/ZSM-5 catalyst: (i) carbidic carbon of Mo<sub>2</sub>C (282.7 eV), (ii) hydrogen-poor (sp-type) pregraphitic carbon (283.5 eV), and (iii) graphitic

carbon (284.6 eV). The authors observed that the sp-type carbon was mainly on the outer surface of zeolite, whereas graphitic carbon was predominantly inside the channels. They proposed that only the sp-type carbon that increased in content during the reaction is responsible for the deactivation of Mo/HZSM-5 catalyst in methane dehydroaromatization. In our study, the used catalyst was flushed with inert gas and a majority of hydrogen-poor pregraphitic carbon could be blown away. As depicted in Figure 13, with prolonged reaction time (5.5 to 41 h), the peak corresponding to graphitic carbon (284.6 eV) increases in area (from ca. 14075.6 to 19023.5 a.u.), and the peak attributed to C-Br species (287.0 eV) changes from 3966.8 to 4546.0 a.u. It is hence regarded that with time-on-stream, both the graphitic carbon and C-Br species increase in content, and serious deactivation is mainly due to the rise of stubborn graphitic carbon inside the channels.

[Figure 13]

### **3.3 Reaction mechanism**

Svelle et al. <sup>[40]</sup> studied the conversion of methyl halide into hydrocarbons over H-SAPO-34. They deduced a reaction mechanism that is similar to that of methanol to hydrocarbon (MTH) reaction. The MTH reaction is generally believed to proceed via a “hydrocarbon pool” mechanism with polymethylbenzenes as major substance in the pool. According to the mechanistic scheme, the formation of lower olefins (ethene, propene, and butenes) proceeds through continuous methylation and dealkylation of the aromatic reaction centers. Svella et al. <sup>[40]</sup> performed theoretical (modeling) studies

that confirmed the feasibility of the mechanism for the conversion of methyl halide into hydrocarbons. Nonetheless, there are other mechanisms proposed for the direction aromatization of low-carbon hydrocarbons where low-carbon olefins ( $C_2^=$ ,  $C_3^=$ ,  $C_4^=$ ) are dominant products [41,42,43]. In view of the fact that aromatics are the main products in our study, we believe that the reaction mechanism of  $CH_3Br$  aromatization over  $PbO/HZSM-5$  should be somewhat different from the ones mentioned above.

During  $CH_3Br$  aromatization over  $PbO/HZSM-5$ , aromatics are the main products and propane and butane are dominant in the gas phase. It is noted that the amount of linear and branched  $C_5$ ,  $C_6$ ,  $C_7$  and  $C_{7+}$  hydrocarbons are produced in small (negligible) amounts. We consider that the “hydrocarbon pool” mechanism is applicable and C propagation is fast. Over  $MgO/HZSM-5$  [30] and  $PbO/HZSM-5$ , one can see that there is no significant difference in  $CH_3Br$  conversion but production of aromatics is poor over the former. Therefore, it is considered that  $CH_3Br$  can be activated by both basic and acidic sites, and acidic sites are indispensable for aromatic formation through steps of C propagation and alkylation. Based on the catalytic and characterization results of  $HZSM-5$  and  $PbO/HZSM-5$  catalysts, one can deduce that the cyclization of linear hydrocarbons formed in the reaction is facilitated by  $PbO$ . It is known that strong acidic sites enhance surface coking. To avoid macromolecules in coking, the catalyst should possess proper acidity and micropores. Much work is underway to disclose the reaction mechanism of  $CH_3Br$  aromatization as well as the role of  $PbO$  in molecular level.

[Scheme 2]

### ***3.4 Catalyst deactivation***

The results of XRD analysis clearly indicate that there is no change of HZSM-5 framework during the CH<sub>3</sub>Br aromatization reaction. Since the spent catalyst can be reused after reactivation, the structure of the catalyst should be stable under the adopted reaction conditions. It is observed that the rate of decline in surface area and pore volume of PbO/HZSM-5 in the first 5.5 h is higher than that within the 5.5 - 41 h period. From the results of TG analysis, one can see that the amount of deposits after 41 h is slightly larger than that after 5.5 h. Hence the formation of deposits is quick at the beginning and then becomes gradual with time-on-stream. The deposited carbon species cover active sites and block HZSM-5 channels, making the active sites less inaccessible. Based on the results, we deduce that the cause of catalyst deactivation is coking.

It is known that the formation of carbon deposits is influenced by the structure and acid-basic nature of catalyst. Also, the HZSM-5 catalysts with micropores show much better catalytic performance than those using mesoporous metal oxides as support. It is apparent that the accumulation of carbon deposits in the micropores is less likely than in the mesopores. As to the effect of surface acidity, it has been regarded that strong acid sites enhance coke deposition, e.g., transformation of methanol to aromatics, aromatization of low-carbon hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>), etc.

Also, catalyst deactivation can be directly related to the amount of acid sites<sup>[44,45,46]</sup>. In our study, we observed that the HZSM-5 catalyst with lower Si/Al ratio shows poorer stability. In addition, the rise of reaction temperature or space velocity of reactant promotes coking. Indeed, a proper control of surface acidity is a way to improve catalytic efficiency by lowering the amount of surface deposits.

#### **4. Conclusion**

It was found that 5wt%-PbO/HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=70$ ) calcined at 450 °C is a good catalyst for the selective conversion of  $\text{CH}_3\text{Br}$  to aromatics. The catalyst is highly active and selective and the yield of aromatics is up to 31.6% at 360°C. The pore structure and surface acidity of the catalyst are main factors that affect the catalytic performance. The deactivation of catalyst is mainly due to carbon deposition.

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## Figure captions

### Scheme 1 Reaction system

1—steel cylinder of compressed nitrogen; 2—release valve; 3—flow displayer; 4—mass flow controller; 5—injector pump; 6—temperature controller; 7—heating equipment; 8—catalyst bed; 9—quartz reactor; 10—collection bottle; 11—ice-water bath; 12—desiccator; 13—ice-bath system; 14—absorption bottle; 15—three-way connection; 16—tail gas.

### Scheme 2 Plausible reaction mechanism over PbO/HZSM-5 catalyst

**Figure 1** Effect of PbO loading on catalytic performance ( $\text{CH}_3\text{Br}$  conversion and aromatic yield) of PbO/HZSM-5 catalysts (Reaction conditions: 3.5g catalyst,  $360^\circ\text{C}$ ,  $\text{WHSV}_{\text{CH}_3\text{Br}} = 1.34 \text{ h}^{-1}$ ,  $\text{N}_2$  flow 5 ml/min).

**Figure 2**  $\text{CH}_3\text{Br}$  conversion over 5wt%-PbO supported on various materials (Reaction conditions: same as Figure 1).

**Figure 3**  $\text{CH}_3\text{Br}$  conversion and aromatic yield over 5wt%-PbO catalysts supported on HZSM-5 molecular sieves with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios (Reaction conditions: same as Figure 1).

**Figure 4** Effect of calcination temperature on performance of 5wt%-PbO/HZSM-5 catalyst (Reaction conditions: same as Figure 1).

**Figure 5** Effect of calcination time on performance (CH<sub>3</sub>Br conversion and aromatic yield) of 5wt%-PbO/HZSM-5 catalyst (Reaction conditions: same as Figure 1).

**Figure 6** Effect of reaction temperature on performance of 5wt%-PbO/HZSM-5 catalyst (Reaction conditions: 3.5g catalyst,  $WHSV_{CH_3Br} = 1.34h^{-1}$ , N<sub>2</sub> flow 5 ml/min).

**Figure 7** Stability and regeneration of catalysts: ☆-HZSM-5; ●-MoO<sub>3</sub>/HZSM-5; ▲- PbO/HZSM-5 before regeneration; ◆-PbO/HZSM-5 after the first regeneration; ◇-PbO/HZSM-5 after the second regeneration (Reaction conditions: same as Figure 1).

**Figure 8** XRD patterns of (a) HZSM-5, (b) fresh 5wt%-PbO/HZSM-5, (c) used 5wt%-PbO/HZSM-5(5.5h), (d) 10wt%-PbO/HZSM-5, and (e) 5wt%-PbO/HZSM-5 after 4 reaction/regeneration cycles.

**Figure 9** (a) TEM bright-field image of 5wt%-PbO/HZSM-5, (b) HRTEM image of HZSM-5, (c) HRTEM image of 5wt%-PbO/HZSM-5; (d) and (e) selected-area EDS analysis of fresh and used 5wt%-PbO/HZSM-5, respectively.

**Figure 10** NH<sub>3</sub>-TPD curves of HZSM-5, 5wt%-PbO/HZSM-5 and 5wt%-MgO/HZSM-5 catalysts with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio = 70.

**Figure 11** CO<sub>2</sub>-TPD curve of 5wt%-MgO/HZSM-5 catalyst with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio = 70.

**Figure 12** TG-DSC curves of 5wt%-PbO/HZSM-5 used at 360°C for (a) 5.5 h, and (b) 41 h.

**Figure 13** C1s spectra of 5wt%-PbO/HZSM-5 after 5.5 and 41 h of reaction.

**Table 1** Conversion, aromatic yield and product distribution over different MO/HZSM-5 catalysts <sup>a</sup>

MO	X (%)	Y (%)	Distribution of liquid products (%)					Distribution of gas products (%)					
			C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10~13</sub>	C <sub>2</sub>	C <sub>2</sub> <sup>=</sup>	C <sub>3</sub>	C <sub>3</sub> <sup>=</sup>	C <sub>4</sub>	C <sub>4</sub> <sup>=</sup>
HZSM-5	93.5	21.5	0.3	2.5	17.9	40.5	38.9	3.5	0.8	66.1	0.6	25.8	3.3
CdO	95.8	9.5	0.6	6.0	27.9	37.2	28.4	9.1	3.8	37.1	4.2	25.7	20.2
Cr <sub>2</sub> O <sub>3</sub>	100.0	11.7	0.8	8.9	43.4	30.9	15.9	12.6	2.6	63.6	0.7	17.2	3.3
V <sub>2</sub> O <sub>5</sub>	94.7	11.9	0.4	0.1	29.4	40.7	29.4	7.1	1.5	30.3	32.4	23.1	5.6
NiO	99.7	12.6	2.1	22.3	42.7	10.6	22.4	5.0	6.3	18.9	11.5	24.3	33.7
MgO	99.5	14.8	2.8	22.1	49.2	12.6	13.4	4.0	2.2	42.6	2.4	38.1	10.7
ZnO	99.3	15.0	2.6	21.1	41.5	17.8	17.1	4.5	4.5	38.8	4.6	36.7	10.8
CaO	99.3	16.5	1.8	21.1	45.0	16.8	15.3	3.9	1.6	62.3	1.1	26.1	4.9
Ce <sub>2</sub> O <sub>3</sub>	99.1	16.7	0.5	7.5	39.2	31.8	21.1	5.5	3.0	65.8	1.2	20.6	3.9
WO <sub>3</sub>	95.2	19.2	0.2	2.6	22.7	43.5	31.0	5.7	1.5	53.5	1.3	30.8	7.3
CoO	99.2	19.3	2.8	20.2	34.0	16.2	26.9	5.4	1.4	56.4	0.8	29.1	6.9
MnO <sub>2</sub>	99.1	19.6	3.1	25.9	42.1	17.3	11.7	9.4	4.2	44.2	4.9	29.6	7.7
Fe <sub>2</sub> O <sub>3</sub>	99.4	20.5	1.7	17.4	45.1	22.6	13.2	6.4	0.8	64.2	0.0	24.3	4.4
Bi <sub>2</sub> O <sub>3</sub>	96.9	25.2	0.4	2.9	19.8	44.4	32.5	6.4	0.8	64.1	0	24.3	4.4
La <sub>2</sub> O <sub>3</sub>	98.3	28.9	0.6	3.7	23.2	46.8	25.8	6.0	3.3	63.5	1.4	22.3	3.5
MoO <sub>3</sub>	98.3	30.7	0.2	2.9	18.5	40.1	38.2	6.1	0.7	74.9	0.4	15.7	2.2
PbO	97.8	31.6	0.4	3.1	18.8	42.4	35.3	3.3	1.5	64.6	1.0	25.2	4.4

<sup>a</sup> Reaction conditions: 3.5 g catalyst, 360°C, WHSV<sub>CH<sub>3</sub>Br</sub> = 0.67 h<sup>-1</sup>, N<sub>2</sub> flow 5 ml/min; X: CH<sub>3</sub>Br conversion (%); Y: aromatic yield (%).

**Table 2** Conversion, aromatic yield and product distribution over 5%wtPbO/HZSM-5 catalysts at different  $WHSV_{CH_3Br}$ <sup>a</sup>.

$WHSV_{CH_3Br}$ ( $h^{-1}$ )	X (%)	Y (%)	Distribution of liquid products					Distribution of gas products					
			(%)					(%)					
			C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10-13</sub>	C <sub>2</sub>	C <sub>2</sub> <sup>=</sup>	C <sub>3</sub>	C <sub>3</sub> <sup>=</sup>	C <sub>4</sub>	C <sub>4</sub> <sup>=</sup>
0.67	97.8	31.6 <sup>b</sup>	0.4	3.1	18.8	42.4	35.3	3.3	1.5	64.6	1.0	25.2	4.4
1.34	94.5	30.5 <sup>c</sup>	0.7	4.6	23.9	46.7	23.8	2.7	2.8	53.4	2.1	30.6	8.5
2.68	89.8	22.1 <sup>c</sup>	0.7	4.9	22.8	47.5	24.1	2.7	4.1	44.4	5.7	27.6	15.5
5.36	68.9	12.5 <sup>c</sup>	0.8	5.1	22.7	48.3	23.1	2.6	4.2	45.3	5.8	28.1	14.0

<sup>a</sup>-Reaction conditions: 3.5 g catalyst, 360°C, N<sub>2</sub> flow 5 ml/min; X: CH<sub>3</sub>Br conversion (%); Y: aromatics yield (%).

<sup>b</sup>-average value on-stream-10h;

<sup>c</sup>-average value on-stream-4h.

**Table 3** Specific surface area and pore volume of fresh and used PbO/HZSM-5 catalysts

Catalyst	$S_{BET}$ (m <sup>2</sup> /g)	Total Pore Volume (ml/g)
HZSM-5	359.5	0.2023
Fresh PbO/HZSM-5	343.7	0.1910
Used PbO/HZSM-5 (5.5h)	234.5	0.1412
Used PbO/HZSM-5 (41h)	144.7	0.0917

**Table 4** Acidity of HZSM-5, 5wt%-PbO/HZSM-5 and 5wt%-MgO/HZSM-5 catalystwith SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio = 70.<sup>a</sup>

Catalyst	Total	$\alpha$		$\beta$		$\gamma$	
	amount of	acid site		acid site		acid site	
	acid sites	amount	P(%)	amount	P(%)	amount	P(%)
	(mmol/g)	(mmol/g)		(mmol/g)		(mmol/g)	
HZSM-5	1.204	0.536	45	0.498	41	0.170	14
5wt%-PbO/HZSM-5	0.886	0.586	66	0.122	14	0.177	20
5wt%-MgO/HZSM-5	1.28	1.28	100	0	0	0	0

<sup>a</sup> Determined by NH<sub>3</sub>-TPD technique. P(%) stands for site amount in percentage.