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A rapid and effective method for evaluating the initial activity of Mo/HZSM-5 catalyst in the methane dehydroaromatization reaction at severe conditions

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ABSTRACT

The very rapid deactivation behavior of Mo/HZSM-5 catalyst in the non-oxidative CH_4 dehydroaromatization needs its cyclic or continuous regeneration operation in a practical reactor system. Design and operation of such a system requires knowledge of the kinetics of catalyst deactivation and its regeneration. The present work reports an easy, rapid and quantitative approach to follow the dynamic variation of the activity of Mo/HZSM-5 in the very initial stage of CH_4 dehydroaromatization at severe conditions. This approach comprises an on-line sampling and storing of a reacted effluent into a number of volume-known loops at intervals from seconds to minutes, and an off-line analysis of the stored samples. With it a nearly continuous dynamic variation in outlet benzene concentration was observed in the first tens of minutes of the reaction for all tested catalysts with Mo loadings ranging from 1.0 to 10 wt.%. Quantitative comparison of the variation with that in the benzene formation rate measured using conventional on-line GC analysis further revealed that the variation actually exhibited the dynamic behavior of the benzene formation activity of catalyst. The approach was subsequently applied successfully to follow the intrinsic maximum activity of Mo/HZSM-5 at severe conditions and in periodic reaction–regeneration operation mode to collect kinetic data for the reactor design.

1. Introduction

In the past two decades concerted efforts have been made to investigate the fundamental aspects of the non-oxidative methane dehydroaromatization over Mo/HZSM-5 [1–9] as well as the industrial applicability of this new reaction [10–15]. In Japan, a combination of the technologies of adding a small amount of CO_2 to methane to suppress coking [16] and of using H_2 to recover the initial activity of Mo/HZSM-5 [17] had led to two successful national process developing projects [14,18].

Case studies conducted in the projects have revealed that this reaction has to be processed at temperatures not lower than 1073 K and space velocities not smaller than 10,000 ml/g-cat/h to obtain performance-acceptable high CH_4 conversion and hourly benzene yield simultaneously. At such severe conditions, however, Mo/HZSM-5 catalyst could lose its activity to a great degree in a few minutes. Thus, the problem arises of how to realize cyclic regeneration of deactivated Mo/HZSM-5 catalyst at short intervals or its continuous regeneration in a practical reactor system. Fluidized bed technology allows an easy, high-rate circulation of solid particles between reactors and therefore can be certainly a solution to the problem [10]. Design and operation of a dual bed circulating fluidized bed reactor system requires knowledge of the kinetics of catalyst deactivation and its regeneration at practical operation conditions. Therefore, there is a practical need to pursue the dynamic variation of the activity of Mo/HZSM-5 in the first few minutes of the reaction at severe conditions. Use of the conventional on-line GC analysis method, however, is unable to accomplish this task because of its too long analysis period.

Here we report for the first time an easy, rapid and quantitative approach to follow dynamic variation of the activity of Mo/HZSM-5 catalyst in the very initial stage of CH_4 dehydroaromatization. This approach consisted of sampling and storing of a reacted effluent into 15 loops of 100 μL on an on-line 16-port sampling valve at intervals from seconds to minutes immediately after the start of the reaction, and analysis of the stored samples by an off-line GC. Therefore, it allowed a nearly continuous monitoring of the rapid variation of outlet benzene concentration in the initial stage of the reaction, which was verified further in the study to exhibit the dynamic variation of the initial activity of Mo/HZSM-5 catalyst itself.

2. Experimental

2.1. Catalyst preparation

A commercial HZSM-5 zeolite (Zeolyst International, Si/Al atomic ratio = 11.5, BET surface area = 350 m^2/g) was used to prepare the four tested Mo/HZSM-5 catalysts with 1, 3, 5, and 10 wt.% Mo

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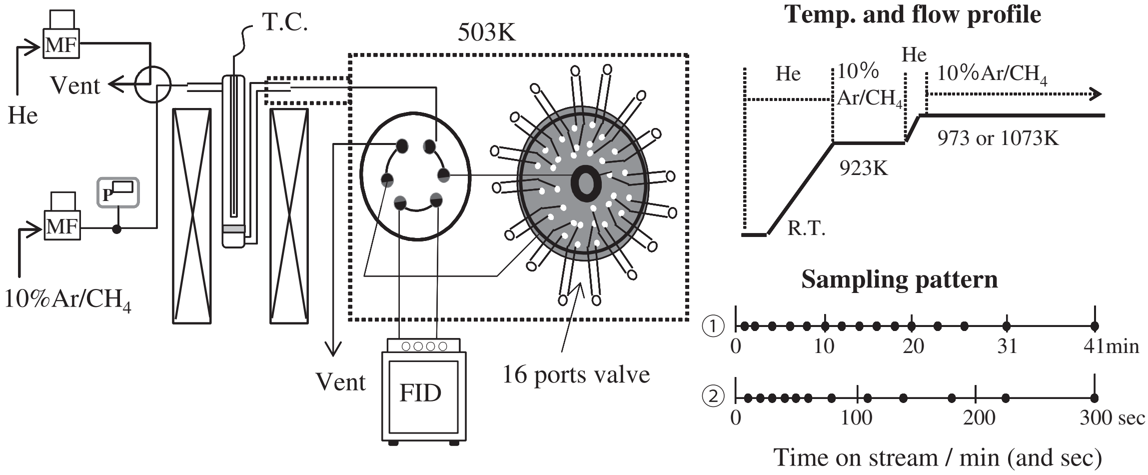

Fig. 1. The schematic of experimental set up, temperature and flow profile and two sampling patterns used.

contents, respectively. The preparation procedure consisted of Mo impregnation on HZSM-5 with an aqueous solution of ammonium heptamolybdate, drying at 383 K for 1 h of the impregnated sample and calcination in air at 773 K for 5 h of the dried sample. The obtained powdery catalysts were pressed, crushed and sieved to particles in sizes of 250–500 μm for use. The Mo contents of the four catalysts were confirmed by ICP analysis to be 0.9, 2.4, 3.9 and 10.3 wt.%, respectively. Their surface areas were also measured using BET method to be 350, 340, 290 and 270 m^2/g, respectively. Furthermore, FT-IR measurement of the catalysts was performed to confirm the dispersion of Mo onto the Bronsted acid sites in the zeolite channels.

2.2. Catalyst test

Tests were conducted in a flow type fixed-bed quartz reactor (8 mm i.d.) at atmospheric pressure and two different temperatures of 973 and 1073 K. Fig. 1 shows the schematic of experimental set up with the detailed configuration of sampling valves, the flow and temperature profile and two sampling patterns used. Briefly, 300 mg of a fresh catalyst packed in the reactor was first carburized in a 17.5 mL/min CH_4 stream at 923 K for 30 min, heated in a He stream to 973 or 1073 K, and then at the temperature subjected to a 10% Ar/CH_4 flow to start the reaction. Subsequently, the effluent from the reactor was sampled at pre-designed intervals from seconds to minutes into 15 loops of 100 μL on an on-line 16-port sampling valve held at 503 K. At the end of the sampling a He stream was flowed through the bed to stop the reaction. Simultaneously, an analysis of the stored samples was carried out by an off-line GC/FID (Shimazu GC-14A) with a Chemipak PH packed column used for the analysis of aromatics in the samples. The samples were introduced to the GC one by one through an on-line 6-port valve between the 16-port valve and GC (Fig. 1). The analysis was performed at a constant column temperature of 423 K and it took in total no longer than 2 h. It was confirmed that no sample leak occurred during the sample-stored periods of time for all 15 loops. The confirmation was made via comparing two sets of analyses of 15 stored gas samples (10% Ar/CH_4), one conducted soon after sampling and the other after the samples were stored in the loops at 503 K for 3 h, and finding little difference in the CH_4 peak areas between the two sets of analyses for each loop. Additionally, absolute amounts of benzene and naphthalene in each of stored 100 μL samples were estimated using external calibration method.

To confirm the reliability and effectiveness of the approach, a set of comparative tests was also conducted with the simultaneous measurement of methane conversion, benzene formation rate and benzene selectivity using the conventional on-line GC analysis method [11].

Additionally, a H_2–CH_4–H_2 switch blank test was conducted to confirm the dead volume of the reactor system. The outlet CH_4 concentration pattern recorded revealed that a 12 second flow of 50 mL/min CH_4 after a H_2 flow at room temperature was enough to purge H_2 out of the reactor completely. This implies that any sample taken 12 s after a flow switching from H_2 to CH_4 at the used flow rate will certainly be of the characteristic of the reacted stream.

3. Results and discussion

3.1. Monitoring of dynamic variation of the benzene concentration using the proposed approach

Fig. 2 compares the variations of the outlet benzene concentration with time on stream measured over all used catalysts at 973 K and 3500 mL/g-cat/h in the proposed approach. In 41 min of the reaction 15 samples were taken and analyzed and therefore the smooth curves were obtained. Considering that only one or two points of data could be obtained in this short reaction period when the conventional on-line gas analysis technique was applied, one has to recognize the effectiveness of the proposed approach in following the rapid variation of outlet benzene concentration in the very initial stage of the reaction.

It is clear from the figure that the variation of outlet benzene concentration depends strongly on Mo loading. At 1 wt.% of Mo loading the benzene concentration reaches the maximum of about

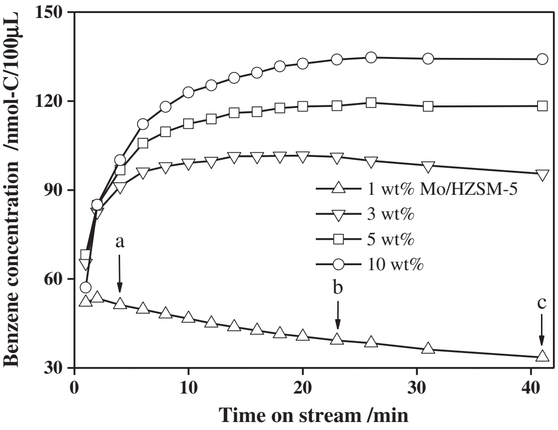

Fig. 2. Variation of outlet benzene concentration with time in the catalytic methane dehydroaromatization at 973 K and 3500 mL/g-cat/h, measured in the proposed approach.

52 nmol-C/100 μL at the second data point (2 min after the start of the reaction) and then decreases slowly with time until the reaction was stopped at 41 min. For the other three catalysts with the Mo loadings of 3, 5 and 10 wt.% respectively, the benzene concentrations, on the other hand, show a similar rapid increase in the first 2 to 6 min, followed by a similar slow increase to their respective maximums. The period of time needed for the catalysts to reach their respective maximum activities became longer with increasing Mo loading, suggesting a longer period of time for the full activation of Mo as its content increased.

Dispersion of MoO_3 onto the Bronsted acid sites in the zeolite channels was confirmed by Pyridine chemisorption on the tested catalysts followed by FT-IR measurements. Obtained spectra revealed a gradual decrease in the intensity of the band 1545 cm^{-1} with the Mo loading increasing from 1 to 10 wt.% [19]. This thus suggests that, as Mo loading increased, there were more Mo species, dispersing into the deep inside of the zeolite channels to create more active sites for CH_4 activation and benzene formation and consequently to lead to an increased maximum benzene formation activity. If a difference in the increase of stream volume through the reaction was assured negligible for the tested catalysts, the variations observed here in the outlet benzene concentration with time would exhibit the dynamic variations of the benzene formation activities of the tested catalysts. This implies that the proposed approach actually allows a quantitative comparison of the very initial benzene formation activities of different Mo/HZSM-5 catalysts in the methane dehydroaromatization.

The cause of the 1 wt.% Mo/HZSM-5 showing the lowest activity was pursued using NH_3-TPD and FT-IR techniques. Obtained NH_3-TPD patterns and IR spectra [19] suggested that this catalyst had more Mo-unoccupied Bronsted acid sites than the others (fewer Mo sites), and thus it was concluded that its insufficiently dispersed Mo sites, over which the activation of CH_4 to CHx and then C_2 intermediates took place, must be responsible for its low benzene formation activity [11].

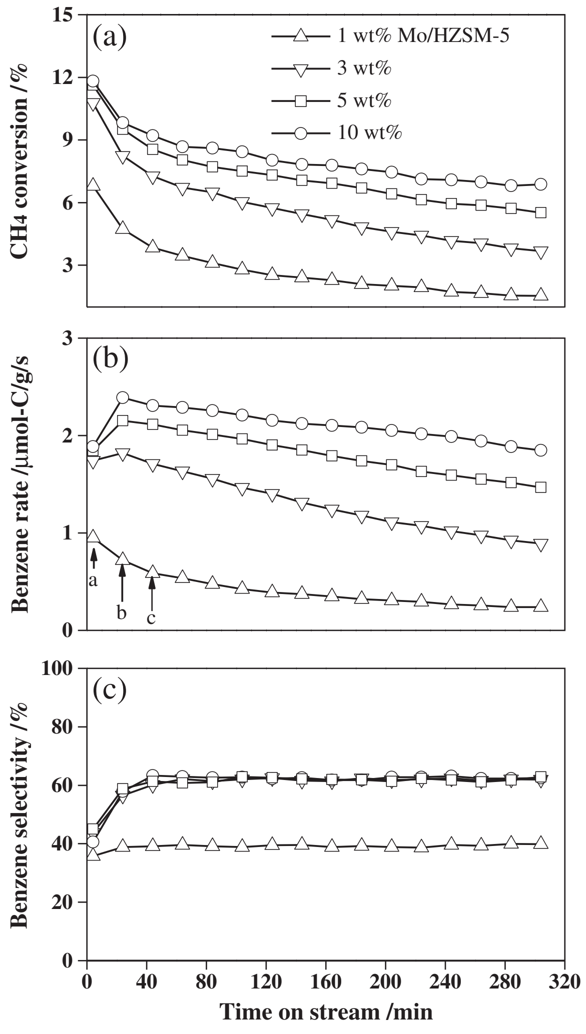

Fig. 3. Effect of Mo loading on the catalytic performance of Mo/HZSM-5 in the methane dehydroaromatization at 973 K and 3500 mL/g-cat/h, evaluated using conventional on-line analysis method.

3.2. Evaluation of catalytic performance in conventional on-line GC analysis method

To verify the above deduction another set of tests with longer time was performed at the same temperature and space velocity but with reacted effluents being analyzed via the conventional on-line analysis method [11]. Fig. 3 shows the obtained time-courses of CH_4 conversion, benzene formation rate and benzene selectivity, respectively. The maximum benzene formation rates are in the order of 10% Mo/HZSM-5 > 5% Mo/HZSM-5 > 3% Mo/HZSM-5 Mo ≫ 1% Mo/HZSM-5, which is in good agreement with that of the maximum outlet benzene concentration observed in Fig. 2. This indicates that monitoring of the variation of outlet benzene concentration in the initial stage of Mo/HZSM-5 catalyzed methane dehydroaromatization is actually measuring the dynamic variation of the initial activity of the catalyst.

To make more quantitative the above comparison, the data at 4, 24 and 44 min, which were labeled as a, b and c in Figs. 2 and 3(b), respectively, were further analyzed. Concretely, the relative benzene concentrations at 4, 24 and 44 min in Fig. 2 and the relative benzene formation rates at the same time points in Fig. 3(b) were estimated, respectively, for all the tested catalysts. As can be seen from Table 1, at each comparative point the difference between the relative benzene concentration and the relative benzene formation rate is not greater than 2% in all cases. This excellent agreement strongly suggests that the outlet benzene concentration curves in Fig. 2 exhibit essentially the dynamic variations of the initial benzene forming activities of the tested catalysts in the methane dehydroaromatization reaction, and thus verify the effectiveness of the proposed approach in quantitative evaluation of the initial activity of Mo/HZSM-5 catalyst.

3.3. Measurement of the maximum benzene forming activity at 1073 K and 10,000 mL/g/h

Because of its variable, short sampling intervals the proposed approach can certainly be used to pursue the intrinsic maximum benzene formation activity of Mo/HZSM-5 catalyst at any severe condition. As shown in Fig. 4(a), at 1073 K and 10,000 mL/g-cat/h there appeared no stable activity period for serious coking and the maximum benzene concentration was observed at approximately 6 min after the start of the reaction. With the conventional on-line analysis method, on the other hand, the maximum benzene formation rate was falsely measured to be at the first sampling point (4 min after the start of the reaction, Fig. 4(b)). By varying the timing for the first sampling one can find out the true maximum benzene formation activity via the conventional approach, but accomplishing this task is

Table 1
The relative benzene concentration ($R_{conc.}$) and the relative benzene formation rate (R_{rate}) estimated from Figs. 2 and 3(b) and at the times of 4, 24 and 44 min, respectively.

Mo loading	a (4 min)		b (24 min)		c (44 min)	
	$R_{conc.}$	R_{rate}	$R_{conc.}$	R_{rate}	$R_{conc.}$	R_{rate}
1%	50.4	51.2	30.1	29.3	25.5	25.0
3%	92.2	91.2	76.2	75.5	72.1	71.2
5%	97.8	96.6	90.2	88.4	90.4	89.2
10%	100	100	100	100	100	100

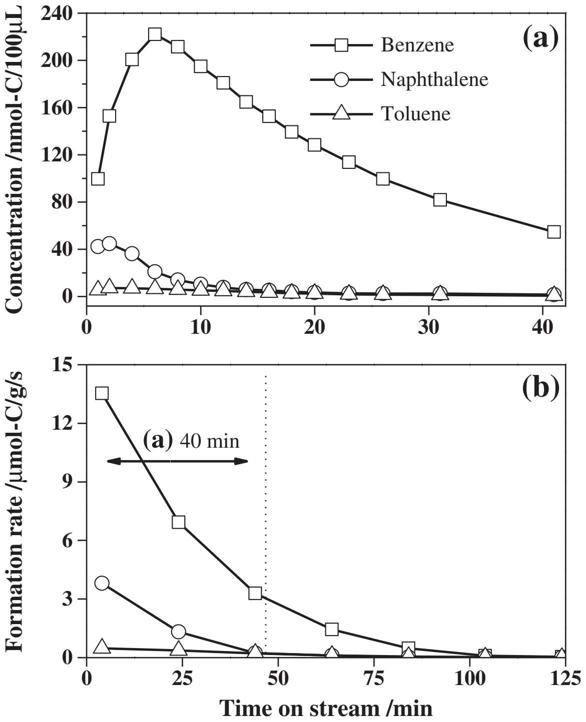

Fig. 4. Time dependences of the benzene formation activity of 5% Mo/HZSM-5 in the methane dehydroaromatization at 1073 K and 10,000 mL/g-cat/h, (a) measured in the proposed approach and (b) measured using the conventional on-line analysis method.

certainly time-consuming. The true maximum benzene forming activity existing in the very initial stage of the reaction could not be easily followed by the conventional on-line GC analysis method, indicating inapplicability of the method for the evaluation of the catalytic activity of Mo/HZSM-5 at rapidly deactivating conditions.

3.4. Following of the maximum benzene forming activity under periodic CH_4–H_2 switching operation at 1073 K and 20,000 mL/g/h

Mo/HZSM-5 catalyst shows a remarkably improved stability in periodic H_2–CH_4 switching operation mode [17]. In this mode Mo/HZSM-5 experiences cyclic exposures to H_2 for its regeneration and therefore its catalytic behavior might vary with the increasing number of cycles. With the proposed approach such variations are also easily pursued. Fig. 5 compares three time-courses of the concentrations of outlet benzene and naphthalene recorded during the 5 min CH_4 exposures of three different cycles (the 2nd, 8th and 14th) in a 5 h periodic 5 min CH_4–10 min H_2 switch test. With the increase in the number of cycles both the maximum outlet benzene concentration and the time needed to reach the maximum became lower and shorter, respectively. While the gradually decreased maximum benzene concentration with the increase in the number of cycles surely suggests a graduate deactivation of the catalyst under periodic operation, the slightly shortened time to attain the maximum might record dynamic variation of the deactivating process itself. The time recorded here to reach the maximum at the three cycles reduced from about 60 to 40 s, but they are all still 3–5 times longer than required for a full purge of H_2 out of the reactor system by CH_4 at the tested flow rate (about 12 s confirmed by the blank test described in the Experimental). Thus it can be concluded that the data in Fig. 5 fully exclude the influence of residual H_2. That is, the rapid increase of outlet benzene concentration in all the cases in the first minute in the figure surely reveals the dynamic behavior of the activity after cyclic H_2 regeneration.

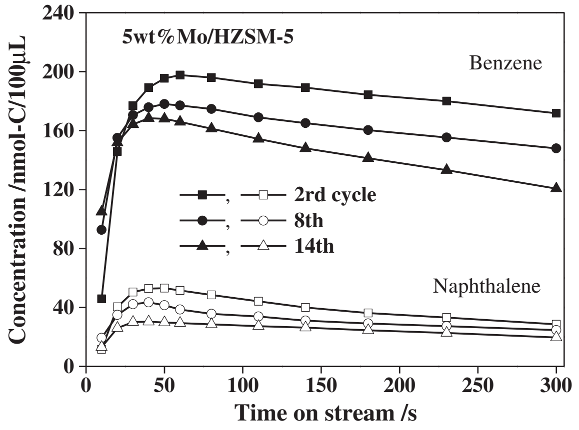

Fig. 5. Variations of outlet benzene and naphthalene concentrations with time in the 5 min CH_4 exposures of three different cycles of a 5 h periodic 5 min CH_4–10 min H_2 switching test at 1073 K and 20,000 mL/g-cat/h.

In addition to provide information about when the catalyst will reach its maximum activity under H_2–CH_4 switching operation, the curves in Fig. 5 also indicate when the catalyst must be subjected to regeneration. Presume that it is essential to keep a catalyst exhibiting no less than, for example, 90% of its maximum activity in the CH_4 exposure period (the reaction period) for operation of a practical reactor system. Thus it is clear from the data for the 2nd cycle in Fig. 5 that the duration of CH_4 exposure in each reaction–regeneration cycle should not be longer than 5 min, that is, the catalyst must be regenerated at 5 min intervals at the used condition. In a two bed catalyst-circulating fluidized bed reactor system [10] this short period of time actually indicates the average residence time of catalyst particles in its CH_4 converter. That is, the proposed approach can also be used to determine the average residence time of catalyst particles in either CH_4 converter or H_2-regenerator of a two bed circulating fluidized bed reactor system, which is one of the most important factors to be primarily considered in the reactor and process design.

4. Conclusion

As demonstrated all above, the proposed approach enables a rapid and quantitative evaluation of the very initial activity of Mo/HZSM-5 catalyst at severe conditions and in periodic CH_4–H_2 switching operation mode. Its application to the activity evaluation of any modified Mo/HZSM-5 catalyst at severe operation conditions, for example, at temperatures and space velocities up to 1173 K and 60,000 mL/g/h, respectively, certainly speeds up the development of industrially applicable catalysts for the reaction [19]. With the help of a second on-line 16-port sampling valve, the approach can also allow an easy acquisition of the intrinsic kinetic data of the catalytic system at severe conditions [20], which includes CH_4 conversion, maximum benzene formation rate and catalyst deactivation rate, all primarily necessary for the reactor and process design.

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