Catalysis Today 185 (2012) 41–46

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Improving effect of Fe additive on the catalytic stability of Mo/HZSM-5 in the methane dehydroaromatization

Yuebing Xu[a,b], Jide Wang[a], Yoshizo Suzuki[b], Zhan-Guo Zhang[b,*]

[a] Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education, Xinjiang University, Urumqi 830046, China
[b] National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569 Ibaraki, Japan

ARTICLE INFO

Article history:
Received 20 May 2011
Received in revised form 9 August 2011
Accepted 16 September 2011
Available online 7 October 2011

Keywords:
Methane dehydroaromatization
Mo/HZSM-5
Metal additives
Carbon nanotube

ABSTRACT

The promotional effects of eight kinds of transition metal additives (0.5 wt%) on the activity and stability of 5 wt%Mo/HZSM-5 were screened at 1073 K and 10,000 mL/g/h in a continuous CH_4 feed mode. Only Fe was observed to improve the activity stability. Subsequently, confirmation tests were performed with other three Fe-modified catalysts containing 0.3, 1.0 and 2.0 wt% of Fe in the same continuous operation mode and also with the 0.5 wt%Fe–5 wt%Mo/HZSM-5 under periodic CH_4–H_2 switch operation for 1650 min. It was confirmed that Fe indeed enhanced the stability of Mo/HZSM-5 catalyst. Then, TPO, TG and BET measurements and SEM observations were performed for almost all spent samples to gain insight into the promotion mechanism of Fe additive. The results revealed that over short time frames in the continuous CH_4 feed mode the formation of Fe-induced carbon nanotubes is the origin of its promotional effect, while under the long-term periodic CH_4–H_2 switch operation the catalytic involvement of Fe in the surface coke removal during the H_2 flow periods is the main cause of Fe-modified catalyst being much more stable than the unmodified Mo/HZSM-5 catalyst

1. Introduction

Mo/HZSM-5 has been demonstrated to be a promising catalyst for the non-oxidative, direct conversion of methane to benzene, a basic aromatic feedstock for the petrochemical industry. However, its rapid deactivation in the reaction due to serious coke formation hinders its practical application. Therefore, over years the problem of how to suppress coke formation over Mo/HZSM-5 and improve its activity stability has been a main subject of the studies on the title reaction. Accordingly, a number of approaches have been attempted to tackle this problem. These include synthesis and use of HZSM-5 with hierarchical structure to improve the diffusivities of formed aromatics diffusing out of HZSM-5 crystals [1], modification of the surface or bulk Si/Al atomic ratio of HZSM-5 to lower the concentration of coking sites [2], addition of oxygen-containing gases to methane feed to gasify instantaneously the coke formed on active sites [3–5], and doping of a second metal promoter to Mo/HZSM-5 catalyst [6].

Compared with the former three approaches, the last one lacks a distinct theoretical ground and is based on the "trial and error" strategy. Probably for this reason, almost all normally encountered transition metals have been tested as promoters. Of them Fe and Co are most investigated. However, no consistent conclusion was reached. For example, Ichikawa and co-workers showed that the introduction of either Fe or Co to a 3 wt%Mo/HZSM-5 increased its activity and stability with less coke formation at a condition of 973 K and 1440 mL/g/h [7]. On the contrary, Kubota et al. showed that the addition of a second metal of Fe, Co, Cr, Ga or In into a 5 wt%Mo/HZSM-5 led to a lower activity for a decreased Mo dispersion at 973 K and 7500 mL/g/h [8]. In between, Burns et al. showed that the promotional effect of dopants on the activity of a 3%MoO_3/HZSM-5 occurred for Fe^{3+}, Al^{3+} and Ga^{3+} but not for Co^{2+} at 973 K and 1200 mL/g/h [9]. Note that these studies all were performed at 973 K. The discrepancies exemplified here may result from different catalyst preparation procedures, different Mo contents and M/Mo atomic ratios in catalysts or uses of different space velocities, which all have been confirmed to have a strong influence on the activity and stability of Mo/HZSM-5 catalyst [6].

As for the promotional effect of Fe additive, Ichikawa et al. suggested that the possible formation of FeMo binary sites might be responsible for, but no such binary phase was detected by XRD technique for a Fe-modified 6 wt%Mo/HZSM-5 [10]. Recently, Masiero et al. reported the formation of $Fe_2(MoO_4)_3$ in a Mo4Fe1 (1 wt%Fe–4 wt%Mo/HZSM-5) catalyst calcined at 873 K for 6 h, but the XRD pattern of their Mo_8Fe_2 catalyst seemed to suggest the formation of an Fe oxide rather than $Fe_2(MoO_4)_3$ [11]. Considering that normally used impregnation conditions do not allow an easy entry of Fe^{3+} into the HZSM-5 channels, we believe that there would be little possibility of formation of any FeMo binary phase

---

* Corresponding author. Tel.: +81 29 861 8091; fax: +81 29 861 8209.
E-mail address: z.zhang@aist.go.jp (Z.-G. Zhang).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.09.026

inside the zeolite channels, where benzene is thought to form. If this is the case and Fe promoter is confirmed to be really effective for the title catalytic system, there will be a need to reexamine its promotion mechanism.

Additionally, there is a need to examine the promotional effect of metal additives at higher temperatures and space velocities in order to find a practically applicable catalyst. Since the title reaction is equilibrium limited and its equilibrium conversion is only about 11% at atmospheric pressure and 973 K, a possible high operating temperature is essential for realizing an acceptable high methane conversion and hourly benzene yield simultaneously. But even so, to our best knowledge, no other group than ours performed the reaction at 1073 K and space velocities of >10,000 mL/g/h [12–14].

In this work the promotional effects of eight kinds of transition metal additives on the activity and stability of 5 wt%Mo/HZSM-5 were first screened at 1073 K and 10,000 mL/g/h in a continuous CH_4 feed mode. Subsequently, the promotional effect of Fe was examined in detail with other three Fe-modified catalysts containing 0.3, 1.0 and 2.0 wt% of Fe in the same operation mode and also with a typical Fe-modified catalyst under periodic CH_4–H_2 switch operation for 1650 min. At last, SEM observations, and TPO, TG and BET measurements were performed for almost all spent samples and the possible promotion mechanisms of Fe additive were discussed in detail based on the finding that carbon nanotubes form only over the Fe-modified catalysts.

2. Experimental

2.1. Catalyst preparation

All 0.5 wt%M–5 wt%Mo/HZSM-5 catalysts (M = Cr, Mn, Fe, Co, Cu, Zn, Ru or Pd) were prepared by impregnation of a HZSM-5 (Si/Al = 15, Zeolyst) with the aqueous mixtures of Ammonium Heptamolybdate and the respective nitrates, followed by drying at 383 K over night and calcination in air at 773 K for 5 h. The obtained samples were pressed, crushed, and sieved into a particle size range of 250–500 μm for tests. A 5 wt%Mo/HZSM-5 catalyst and another three Fe-modified catalysts with 0.3, 1.0 and 2.0 wt% of Fe were also prepared in the same procedure. The Mo content of the 5 wt%Mo/HZSM-5 was confirmed by ICP analysis to be 4.9%.

2.2. Catalyst characterization

NH_3-TPD measurements of all catalysts were conducted in an auto-controlled flow reactor system (TPD-1, Bel.). 50 mg of a catalyst sample was used for each measurement. After heat-treated in a He stream at 773 K for 1 h, the sample was exposed at 403 K to 40 Torr ammonia for 30 min. Subsequently it was heated in He to 923 K at a rate of 10 K/min to obtain the NH_3-TPD pattern. The same TPD apparatus was also used for TPO measurements of all spent samples. 30 mg of a spent catalyst sample was treated in a He stream at 313 K for 60 min and then heated in a 50 mL/min flow of 10%O_2/He to 973 K to obtain the TPO profile. The amounts of coke accumulated on the spent samples were determined by thermal gravimetric (TG) analysis (TG/DTA6200, Seiko Instruments Inc.). About 10 mg of a spent sample was heated in an air stream from 303 K to 873 K at a rate of 10 K/min to obtain the weight loss profile. SEM observations of all spent samples were conducted using a FESEM (Hitachi S-4300) with the maximum magnification of 100,000×. For some catalysts and spent samples, N_2-adsorption measurements were performed in a BET apparatus (Belsorp-18A, Bel.) at 77 K to evaluate their micropore surface areas and micropore volumes.

2.3. Catalyst evaluation tests

All screening tests were carried out in a U-type fixed-bed quartz reactor (8 mm i.d.) under a condition of atmospheric pressure, 1073 K and 10,000 mL/g/h. A sampler composed of one six-way valve and one 16-port valve was configured just at the outlet of the reactor to realize on-line sampling at any given point of time. The detailed configuration of the sampler and two exemplified sampling patterns are given in a previous paper [15]. In each test approximately 150 mg of a catalyst sample was carburized at 923 K in a 17.5 mL/min CH_4 stream for a pre-determined period of time, heated in a H_2 stream to 1073 K, and then subjected to a CH_4 flow at the temperature to start the reaction. The effluent from the reactor was sampled at pre-designed intervals from seconds to minutes into 15 100 μL loops on the 16-port valve. Analysis of the stored samples was conducted using a GC with FID detector to obtain the variations of the concentrations of formed benzene and naphthalene.

Tests in the periodic CH_4–H_2 switch operation mode were conducted in a similar reactor system. The reacted effluent from the reactor in CH_4 flow durations was on-line sampled using a 10-port valve kept at 503 K and analyzed by two gas chromatographs [16]. 10 vol% of Ar contained in the feed CH_4 was used as internal standard to estimate CH_4 conversion. The rates of formation of benzene and naphthalene were estimated using external calibration method.

3. Results and discussion

3.1. Characterization

Fig. 1 compares the NH_3-TPD profiles obtained for the HZSM-5, 5 wt%Mo/HZSM-5 and all metal-modified 5 wt%Mo/HZSM-5 catalysts. Similar to other HZSM-5 samples, the zeolite sample used in this work exhibits two NH_3 desorption peaks centered at 520 and 700 K. These peaks are ascribed to NH_3 molecules adsorbed on Lewis and Brønsted acid sites [17], respectively. For the 5 wt%Mo/HZSM-5 the intensity of the higher temperature NH_3-desorption peak is obviously lower than that of the zeolite sample. This confirms that Mo indeed migrates and interacts with Al–OH–Si groups in the zeolite channels during the catalyst preparation to reduce its Brønsted acidity [18,19]. Such a decrease was also confirmed by measurements of the FTIR spectra of pyridine on the two samples [13]. Assuming that Mo is anchored to the channel Brønsted acid sites in a uniform mode [20,21], the reduction observed here in the intensity of the higher temperature NH_3-desorption peak actually reflects the number of well-dispersed Mo sites in the catalyst. Thus, the difference in the Brønsted acidity between the zeolite sample and the 5 wt%Mo/HZSM-5 catalyst was used to estimate the ratio of Mo to unoccupied Brønsted acid sites of the catalyst. It was found to be 4.5, close to the suggested best ratio for a good catalyst for the title reaction [22].

All metal-modified catalysts, except for 0.5 wt%Ru–5 wt%Mo/HZSM-5, exhibit the NH_3-TPD patterns almost identical to that of the 5 wt%Mo/HZSM-5. That is to say, the 5 wt%Mo/HZSM-5 and all but Ru-modified catalyst have the same low Brønsted acidity. This suggests that the introduction of any of the second metals except Ru neither increases Mo dispersion nor inhibits the migration of Mo species into the zeolite channels occurring in the calcination step of catalyst preparation. A possible explanation for this is that all metal additives were impregnated on the external surface of the zeolite. For the 0.5 wt%Ru–5 wt%Mo/HZSM-5 the intensity of the NH_3-desorption peak in the region of 600–800 K is obviously lower than that of the 5 wt%Mo/HZSM-5. Apparently this suggests that the presence of