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A Transient Behaviour in the Initial Production of Aromatic Compounds from Methane Catalyzed by Mo/HZSM-5

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Abstract The production of aromatic compounds directly from methane using catalysts based on zeolite HZSM-5 impregnated with molybdenum was investigated using a flow reactor at 750 °C. Main products were benzene and naphthalene as well as toluene and others like azulene in smaller amounts. Naphthalene appeared after benzene following an induction period suggesting a consecutive reaction path. A transient behavior in the production of naphthalene was observed along the time on stream, being benzene practically the only product at the steady state. The transient behavior disappeared when increasing contact time, which produced more naphthalene at the expense of benzene.

Keywords Methane · Methane activation · Dehydroaromatization · Mo/HZSM-5

1 Introduction

The increasing demands for liquid fuels and the existing large world reserves of natural gas make attractive the direct transformation of methane into more desirable liquid hydrocarbon feedstock. Though not yet industrially developed due to thermodynamics limitations of the chemical reaction, the process appears to require a bi-functional catalyst capable to first activate methane to produce hydrocarbon rearrangement into larger hydrocarbon molecules.

Previous works [1–5] have shown that promising catalysts for the dehydroaromatization of methane (MDA) results from the combination of a transition metal with a zeolite. Particularly, molybdenum impregnated on a HZSM-5 zeolite support is one of the catalyst most studied.

Earlier studies on the interaction of Mo with Si–Al oxide supports [6,7] suggest that after impregnation, a subsequent calcination may produce superficial molybdenum aluminate causing desaluminization of the alumino silicate besides the modification of surface acidity.

After impregnation and calcination, treating the Mo/HZSM-5 catalyst with CH4 at high temperature causes substantial modifications involving migration of Mo species either by surface movement or gas-phase transport, as well as transformation of MoOx species into MoCx species [5].

The unusual resistance to coking cited for the HZSM-5 zeolite [8] could probably be one of the key factors for the functioning of Mo/HZSM-5 catalysts in MDA reaction. However, the reaction mechanism on this bi-functional catalyst is not well understood and several complicated factors are present; for example: mass transfer of product molecules involved may be difficult inside the zeolite channels. Indeed, ring diameters of benzene and naphthalene (7–10 Å) are similar or even wider than the channel diameter (around 5–7 Å in HZSM-5). Furthermore, diffusion of surface intermediates must take place if sites with different functions are not closely located. Indeed, two reaction steps involving two different sites have been suggested [4], one for methane activation and initial C–C bond formation (Mo sites) and another for aromatic ring formation (H^+ sites), reporting maximal MDA efficiency for the ratio of (Mo sites)/(H^+ sites) close to unity, which probably depends mainly on optimal Mo loading and Si/Al ratio, as well as on the methods for catalyst preparation

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(e.g., impregnation or ion exchange, calcination temperature, etc).

In the present communication, we will be adding more data to the complex MDA catalysis, implicating a catalytic mechanism that produces an initial transient behavior in the reaction product distribution.

2 Experimental

Mo/HZSM-5 catalysts with concentrations of 5, 10, and 15 wt% MoO3 were prepared. In each case, preparation consisted in the impregnation of the HZM-5 zeolite (from Zeochem, SiO2/Al2O3 = 30) with an aqueous solution of ammonium molybdate of known concentration. Impregnation was carried out at 80 °C stirring the liquid-solid mixture until dryness, completing drying in an oven at 110 °C. Thereafter the samples were calcined at 500 °C. Pure MoO3 was prepared from the same ammonium molybdate following same temperature treatment.

A continuous flow reaction system was employed connected with a six-port sampling valve to a gas chromatograph (HP G1800A) equipped with a capillary column and a mass spectrometer detector for product separation and identification. The reactant flow consisted of a mixture of high purity helium (50 mL/min) and methane (50 mL/min) fed at nearly atmospheric pressure to a quartz tubular reactor (10 mm diameter) placed inside of a vertical tubular furnace. Catalyst sample (100 or 500 mg) was placed inside the reactor packed between quartz wool and silica pearls. Reactor outlet and sampling valve were kept at about 300 °C using heating blankets. Reactor temperature was increased from ambient at a rate of 20 °C/min under flowing reactant gas, and "zero" time on stream was assumed at the moment when temperature reached the set value (750 °C). Methane conversion and product selectivity reported below were directly calculated from the chromatographic peak areas.

3 Results and Discussion

Preliminary experiments demonstrated that the zeolite alone and the pure MoO3 (mechanically mixed with the zeolite) both showed not noticeable activity for MDA.

XRD spectra (Fig. 1) show sharp peaks characteristic of the zeolite in all the impregnated samples. Peaks corresponding to orthorhombic MoO3 were noticed clearly in sample with 15% MoO3, but not in the other Mo-impregnated samples.

Figure 2 indicates that there is an initial deactivation respect to methane conversion along time on stream to

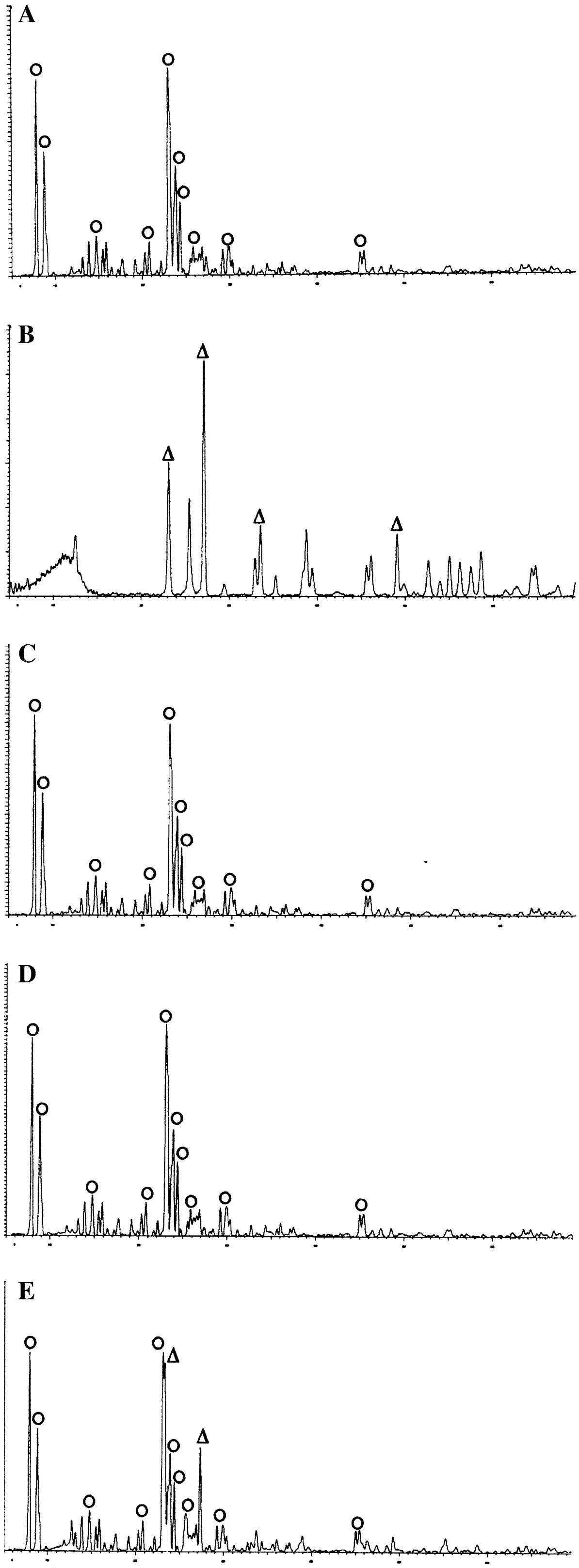

Fig. 1 XRD Spectra (CuKα) (**A**) HZSM5, (**B**) pure MoO3, (**C**) 5 wt%, (**D**) 10 wt%, and (**E**) 15 wt% MoO3

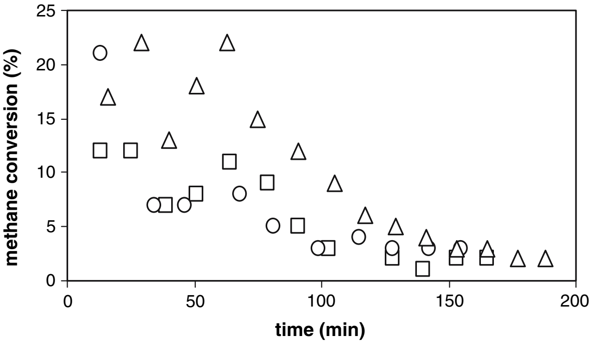

Fig. 2 Methane conversion at 750 °C using Mo/HZSM5 catalysts (100 mg) with different Mo loadings. (○: 5 wt%, □ : 10 wt%, and Δ : 15 wt% MoO3)

reach an apparent and low steady state activity (less than about 5% methane converted for the three catalyst tested). Benzene, toluene, and naphthalene were the products observed in all cases (Fig. 3), but traces of other aromatic product (azulene, indene, methyl and ethyl naphthalenes) were also detected. Some significant amount of azulene was found only when testing catalyst with 15 wt% MoO3 (Fig. 3C).

An induction period was observed for the naphthalene formation, i.e., naphthalene appeared about 0.5 h after benzene and toluene (Fig. 3). This behavior suggest a consecutive reaction path, i.e., naphthalene formed from benzene and not from methane. A transient behavior appears in all cases shown in Fig. 3, i.e., naphthalene practically disappears after reaching maximum concentration, suggesting that catalyst deactivation apparently affected naphthalene production more drastically than benzene production.

Working with larger contact time (i.e., using 500 mg of catalyst instead of 100 mg) produced more naphthalene at the expense of benzene consumption (Fig. 4). It can also be observed in Fig. 4 that the transient phenomena observed when using lower contact time (Fig. 3) disappeared.

Causes for the transient behavior observed cannot be ascertained yet without further experimental evidences. Nevertheless, one may speculate that benzene desorbed immediately after being formed, but naphthalene stays adsorbed some time before desorbing. The driving forces for the sudden desorption of the naphthalene stored during the induction period could be related to some electron-band properties of solid. For example, a possible mechanism could involve a continuous increase with time on stream of the surface coverage by carbonium ion linked to naphthalene, which remains adsorbed due to electrostatic forces, up to a coverage state where electrons charging solid reach a critical value which activates electron return to surface to neutralize the carbonium ions and therefore, producing desorption. The increase of the contact time probably produces more surface carbonium ion concentration leading to a continuous production of both benzene and naphthalene after a shorter induction period (Fig. 4).

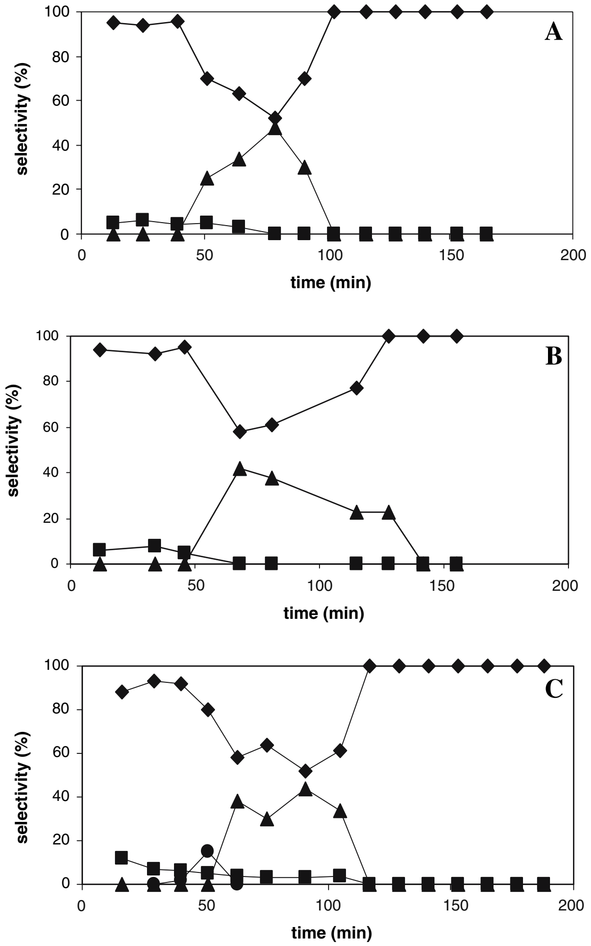

Fig. 3 Product selectivity. (**A**) 5 wt%, (**B**) 10 wt%, and (**C**) 15 wt% MoO3. Catalyst sample: 100 mg. (♦: Benzene, ■ : Toluene, ▲ : naphthalene, ● : azulene)

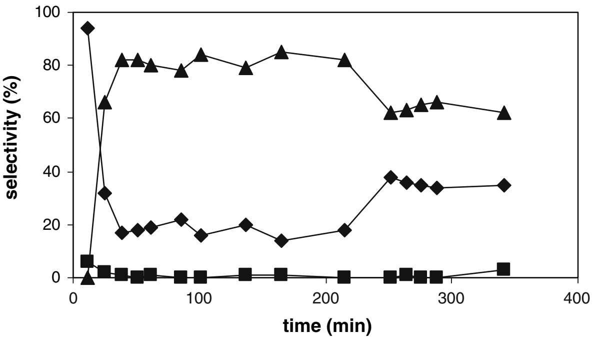

Fig. 4 Product selectivity. Catalyst sample (10 wt% MoO3): 500 mg (keys as in Fig. 3)

The well-known resistance to coking ascribed to the HZSM-5 zeolite [8] is most probably related to the above proposed mechanism. Indeed, naphthalene formation may be an initial step for coke formation, therefore, naphthalene desorption should inhibits catalyst deactivation by coke formation. Accordingly, steady activity after initial deactivation is maintained probably as a result of the ability of the zeolite to impede the irreversible adsorption of large amounts of naphthalene leading to coke formation, hence keeping clear certain extension of the active surface for continuing aromatic production.

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