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The effect of dopants on the activity of MoO_3/ZSM-5 catalysts for the dehydroaromatisation of methane

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Abstract

The effect of a number of dopants – Co^{2+}, Fe^{3+}, Al^{3+}, Ga^{3+} and $P^{(V)}$ – on the catalytic activity of MoO_3/ZSM-5 dehydroaromatisation catalysts has been investigated. Promotional effects were observed with Fe^{3+}, Al^{3+} and Ga^{3+}, whereas $P^{(V)}$ added in the form of phosphomolybdic acid decreased the benzene formation rate. Doping with Co^{2+} was not observed to produce any promotional effects, aside from an initial high conversion and burst of hydrogen which was short-lived. In the case of iron, although the benzene formation rate was close to that for the non-doped parent catalyst in the early stages, benzene formation was enhanced at longer times on stream and the addition of iron was observed to enhance methane conversion, principally through enhanced coke formation. The addition of gallium was found to produce an enhancement of benzene production in the early stages of reaction, but its principal effect was the reduction of hydrogen producing side reactions associated with the formation of coke. In comparing the effects of metal ion addition, it is notable that the impregnation solutions of Fe^{3+}, Al^{3+} and Ga^{3+} are acidic. Possible effects of these dopants such as zeolite dealumination, modification of catalyst acidity and the formation of mixed molybdenum containing phases or re-dispersion of the MoO_3 phase can be advanced as potential explanations for the observed effects.

Keywords: Methane; Dehydroaromatisation; Molybdenum oxide; Molybdenum carbide; ZSM-5; Dopants

1. Introduction

In recent years, the production of benzene by the dehydroaromatisation of methane has attracted a lot of interest, for example [1,2]. The most well-studied catalytic system in this respect is based upon ZSM-5 supported molybdenum oxide. It is believed that during reaction conditions, the active phase of molybdenum is the carbide [3,4], although proposals for oxycarbide phases have also been made. The reaction mechanism is generally considered to proceed via an initial dehydrogenation step to yield an intermediate C_2 hydrocarbon (most frequently argued to be ethylene [5], although acetylene has also been proposed [6]) followed by cyclisation associated with the acid functionality of the zeolite. Key features of the reaction, which is generally run at ca. 700 °C or above with a low space velocity, are that it is potentially equilibrium limited and that the catalyst deactivates on prolonged reaction due to the accumulation of coke. In this respect, there has been intense interest in the enhancement of both activity to allow operation at higher space velocity and suppression of the deactivation process. Doping catalysts with additional metals such as iron or cobalt [7,8] has been reported to retard deactivation and enhance activity and the addition of low levels of gas-phase species such as CO and CO_2 [9,10] has proved beneficial. Within the literature, most attention has been directed towards the production of aromatics and it is somewhat surprising that, with only a few notable exceptions, e.g. [7,10], so little attention has been given to the production of hydrogen, which is expected to be the major product of reaction. In addition to benzene, a range of additional hydrocarbons are produced with C_2 hydrocarbons (particularly ethylene) being the most significant, but reports of the production of toluene, naphthalene and even methylnaphthalene, e.g. [7,8,11] have been made. In this study, the effect of Co^{2+} and Fe^{3+} dopants has been re-investigated and the range extended to include Al^{3+}, Ga^{3+} and $P^{(V)}$.

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2. Experimental

Catalysts were prepared by impregnation of ammonium heptamolybdate onto H-ZSM-5 precursors. In the case of Co, Fe, Al and Ga doped catalysts, an appropriate amount of ammonium heptamolybdate was impregnated onto a H-ZSM-5 (Si/Al = 40) supplied by Catal. The material was then dried at 80 °C for 24 h and calcined in air at 500 °C for a further 16 h. Co, Fe, Al and Ga dopants were added from aqueous solutions of the respective nitrates, followed by drying and calcination as described previously. The parent catalyst was prepared by an analogous procedure, omitting the dopant impregnation step. Phosphorus doped samples were prepared by impregnation of a Zeolist H-ZSM-5 (Si/Al = 50) with an aqueous solution of phosphomolybdic acid, followed by drying at 80 °C for 24 h and calcining in air at 500 °C for a further 16 h. For reference, a non-phosphorus containing MoO_3/Zeolist ZSM-5 was prepared using ammonium heptamolybdate as described above.

Catalyst testing was performed in a fixed bed silica glass microreactor wherein 0.5 g of catalyst in powder form was held centrally within a tube furnace between silica wool plugs. Methane (BOC 99.5%) was flowed over the catalyst at 8 ml min^{-1} and nitrogen (2 ml min^{-1}) was used as an internal standard. The reaction was performed at 700 °C which was measured using a thermocouple attached to the outer wall of the reactor tube. Product analysis was performed on a HP 5890 GC using a combination of FID and TCD with a Poraplot Q column and a Molecular Sieve 13X column, respectively. CHN analysis was performed on catalysts run for 390 min on stream using a CE-440 Elemental Analyser.

3. Results and discussion

Fig. 1 reports the methane conversion of the standard 3% MoO_3/ZSM-5 catalyst over a 350 min timescale. In Fig. 2, data are shown for both the rate of production of hydrogen and that for benzene (the two major products of reaction). The profile shown is generally similar to those reported in the literature for comparable catalysts tested under similar conditions, in that there is an early peak followed by a smooth decline. At the peak of activity, the methane conversion is in the region of 5%, which declines to ca. 3% over the course of the experiment. If hydrogen and benzene were the sole products produced, the ratio of their rates would be expected to be 9. However, as shown in Fig. 3, the ratio is closer to 21 which is indicative of the side reactions occurring. When account is taken of the production of C_2 hydrocarbons, the H_2:C_6H_6 ratio would be expected to be in the region of 13. The ratio of 21 is indicative of the formation of heavier aromatics and/or coke. Since heavier aromatics are generally produced in much lower selectivity than benzene, it is most probable that the major contribution to the higher ratio is from coke formation. This is backed up by carbon analysis on post-reaction samples, reported in Table 1, in which 4.21 wt.% carbon is observed to be deposited after 390 min on stream. If the stoichiometry of the Mo containing phase is assumed as Mo_2C, as is most commonly reported in the literature, this means that ca. 4.08 wt.% C is deposited on the catalyst as coke. In Fig. 3, it is particularly interesting to note the relative constancy of the hydrogen to benzene formation rate ratio, which implies that the benzene formation and hydrogen producing side reactions decline at similar rates.

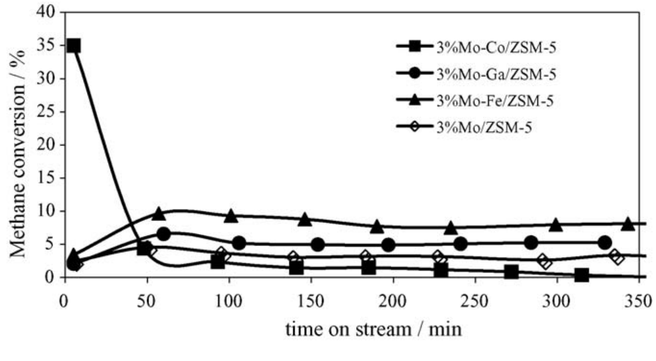

Fig. 1. Methane conversion as a function of time on stream for the parent 3 wt.% MoO_3/ZSM-5 catalyst, and those doped with Co^{2+}, Fe^{3+} and Ga^{3+} (with dopant metal ion/Mo molar ratio of 0.25).

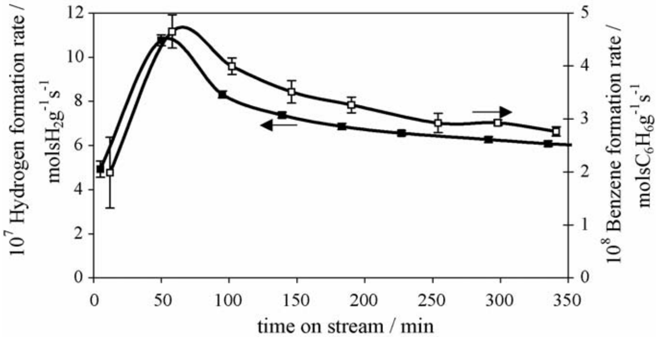

Fig. 2. Benzene and hydrogen formation rates as a function of time on stream for 3 wt.% MoO_3/ZSM-5.

Following the reports of Ichikawa and co-workers [7,8], the effect of the addition of Co and Fe dopants have been investigated and the results are shown in Figs. 1 and 4–6. The level of dopant applied corresponds to that reported to have maximum effect. In the case of cobalt, no significant promotional effect has been observed, aside from an initial burst of activity where hydrogen was observed as a major product and indeed, the presence of cobalt appears to actually

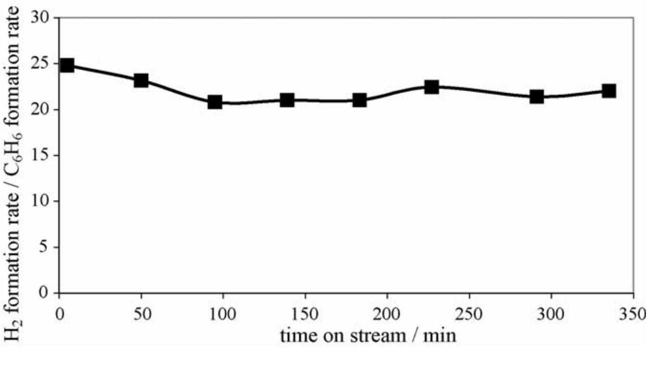

Fig. 3. The ratio of H_2 to C_6H_6 formation rates as a function of time on stream for 3 wt.% MoO_3/ZSM-5.

Table 1
Post-reaction CHN analysis of catalysts

Catalyst	%C	%H	%N
3% MoO_3/ZSM-5	4.21	0.14	–
Co^{2+} doped 3% MoO_3/ZSM-5	5.50	0.15	–
Fe^{3+} doped 3% MoO_3/ZSM-5	5.69	0.15	–
Ga^{3+} doped 3% MoO_3/ZSM-5	3.09	–	–
5% MoO_3/Zeolist ZSM-5	5.70	0.11	–
5% MoO_3/Zeolist ZSM-5 (phosphomolybdic acid precursor)	5.67	0.22	–

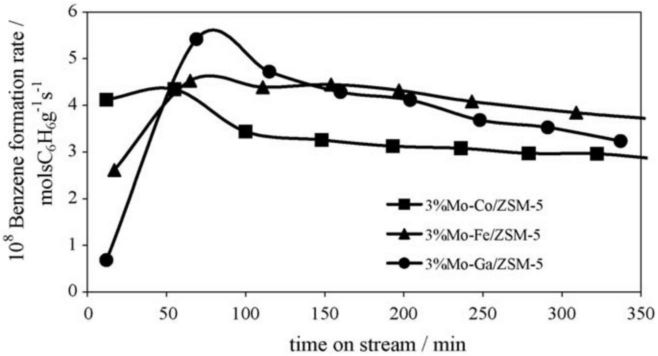

Fig. 4. Benzene formation rates as a function of time on stream for Co^{2+}, Fe^{3+} and Ga^{3+} doped 3 wt.% MoO_3/ZSM-5 (dopant metal ion/Mo atomic ratio = 0.25).

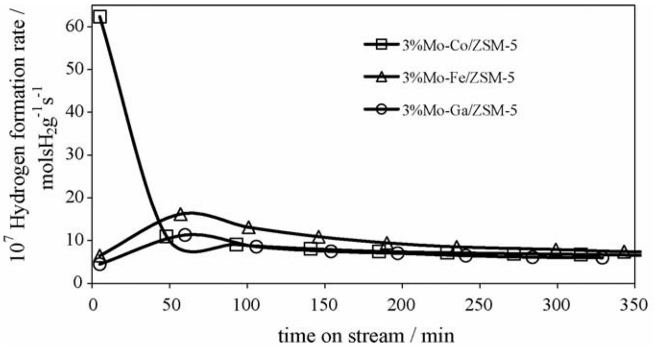

Fig. 5. Hydrogen formation rates as a function of time on stream for Co^{2+}, Fe^{3+} and Ga^{3+} doped 3 wt.% MoO_3/ZSM-5 (dopant metal ion/Mo atomic ratio = 0.25).

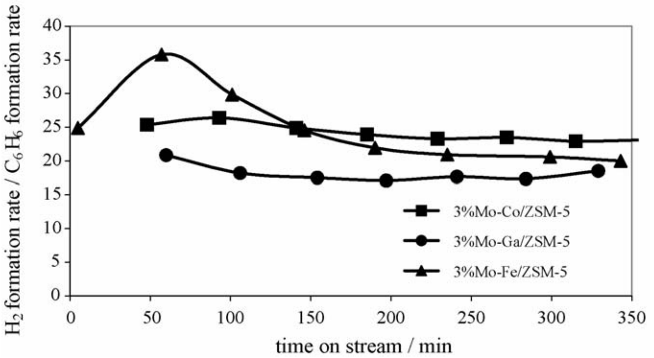

Fig. 6. The ratio of H_2 to C_6H_6 formation rates as a function of time on stream for for Co^{2+}, Fe^{3+} and Ga^{3+} doped 3 wt.% MoO_3/ZSM-5 (dopant metal ion/Mo atomic ratio = 0.25).

suppress benzene formation in the current study. Similar high initial, and rapidly declining, hydrogen profiles have been observed for reduction/carbiding of several metal oxides under similar reaction conditions [12]. In order to probe the lack of a promotional effect of cobalt addition on catalyst behaviour at longer times on stream, a number of variables such as calcination procedure have been investigated, but have not been found to produce significant differences. Iron, however, does enhance activity at longer reaction times. The peak methane conversion corresponds to 10% which falls to ca. 8% over the course of the experiment. Previously, the promotional effect of iron was ascribed to the reduction of coke formation, rather than enhancement of methane conversion. However, the results presented here contradict that interpretation. In addition, the H_2:C_6H_6 formation rate ratio shown in Fig. 6, shows a much more pronounced maximum with a sharper and more continual decline. This is indicative of the fact that hydrogen producing side reactions, such as coke formation, decline at a faster rate than that for benzene production. Indeed, the generally higher ratio evident in Fig. 6 as compared to Fig. 3 may be an indication that the relative formation of coke is in fact higher on the addition of iron. Initially the benzene formation rate profile is similar to that for the parent MoO_3/ZSM-5 catalyst, however, the addition of iron is found to produce beneficial effects at longer times of stream. This may be as a consequence of retarded deactivation or the slow evolution of additional active phases with time on stream. Within the literature, Weckhuysen et al. [13–15] have demonstrated that, in the absence of MoO_3, impregnation of iron oxide alone onto ZSM-5 yields active methane dehydroaromatisation catalysts. The active form of such catalysts has been proposed of comprising dispersed Fe_3O_4 entities on the ZSM-5 matrix. Ichikawa and co-workers [7] have also observed iron containing catalysts to be active, although with very low conversions and low (ca. 20%) selectivity to benzene. This was interpreted on the basis of the promotional effect of iron as being due to the formation of binary Fe–Mo carbides or oxides. In the case of the catalysts studied here, the molybdenum containing phases are too highly dispersed to be observed in powder diffraction studies. It is therefore difficult to comment on whether binary phases are indeed formed, whether there are additive effects on activity between segregated Mo and Fe containing phases or whether the addition of the iron containing dopant is modifying the dispersion of the molybdenum containing component. Future studies, employing Fe and Mo EXAFS will aim to address these issues.

As well as potential differences in the nature of the phases formed with Co and Fe dopants, it is notable that, unlike the case for Co, the impregnation solution would be expected to be significantly acidic in the case of iron (ca. pH 3 versus pH 7 for Co^{2+}). Acidic impregnation, could lead to dealumination of the zeolite framework and this aspect is currently under investigation. Aqueous solutions of aluminium nitrates are also relatively acidic, and accordingly impregnation with Al (to yield a Al/Mo ratio of 0.25) has been performed. To our knowledge, this is the first time that Al doping of MoO_3/ZSM-5 aromatisation catalysts has been reported. Al has been observed to enhance benzene production, but this is not reported here since, although promotion is consistently observed, the magnitude of the promotion has been observed to be variable. The reasons for this, e.g. potential ageing effects, are currently under investigation. However, it is interesting to note that in many reports the formation $Al_2(MoO_4)_3$ phases, which might be anticipated with the use of aluminium dopant, has been associated with low catalytic activity, e.g. [16]. Extraction of framework aluminium by the addition of Mo has been widely reported and it is possible that the further addition replaces some of the lost framework Al. A number of alternative explanations can be envisaged. For example, Al could form active extra-framework species, it could modify dispersion of Mo containing phases, or it could be acting as an acidity modifier which leads to enhancement of activity via a better distribution of molybdenum versus acid sites.

As a consequence of the promotional effects of Al doping, Ga doping has also been investigated. However, compared to aluminium, gallium would be expected to be more reducible under reaction conditions and could exist as, e.g. Ga^+ species. The activity of Ga/ZSM-5 catalysts in the Cyclar process, in which aromatics are formed from C_3 and C_4 alkanes, is well-documented, e.g. [17,18]. The role/nature of the gallium containing phase is currently unclear, with amongst other proposals, facilitated hydrogen desorption being advanced, e.g. [19]. In addition, isotopic studies have indicated that Ga_2O_3 is a very active for CH_4/D_2 exchange [20]. Synergistic effects between Ga_2O_3 and MoO_3 phases have also been documented in alkane oxidation [21,22] in which alkane activation is generally rate determining. It is therefore reasonable to anticipate that Ga doping would have a beneficial effect and this is indeed borne out by the data shown in Figs. 4–6. The peak methane conversion for this catalyst is ca. 6.5% which slowly declines to 5% over the course of the experiment. In addition to promoting conversion, the data shown in Fig. 6 indicate that there is a slight decrease in the H_2:C_6H_6 ratio on gallium addition, which indicates a relative reduction in the hydrogen producing side reactions, such as coke formation. In addition, as seen previously, there is a relative constancy in the ratio, indicating that the benzene producing and hydrogen producing side reactions decrease at similar rates. As reported in Table 1, post-reaction carbon analysis shows 3.09 wt.% carbon which is the lowest amount observed amongst all the catalysts tested.

In the case of the dopants described above, because they are added to the ready-prepared MoO_3/ZSM-5 catalysts, it is difficult to say whether they interact directly with molybdenum containing phases, or whether they form segregated phases having a more indirect effect. It is notable that the dopants which have been observed to have a beneficial effect on catalysis have been prepared from acidic precursor solutions. As discussed, this effect alone could lead to localised dealumination effects on the zeolite framework. However, if these effects occur, they are limited since powder diffraction demonstrates that the zeolite framework structure largely remains intact.

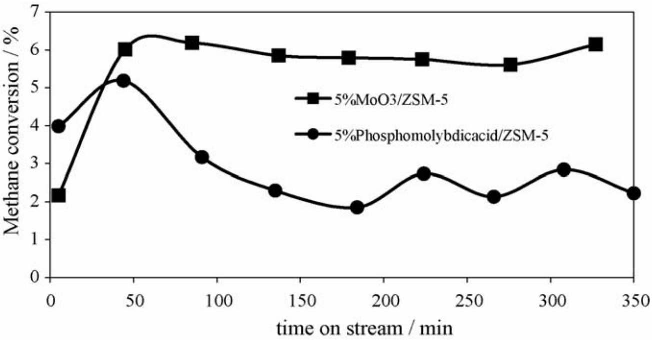

Fig. 7. The conversion of methane over 5 wt.% MoO_3/Zeolist ZSM-5 and 5 wt.% MoO_3/Zeolist ZSM-5 prepared from phosphomolybdic acid (P/Mo atomic ratio = 0.08).

In an attempt to address the issue of acidity and association of the dopant with the molybdenum phase, catalysts have been prepared via phosphomolybdic acid impregnation. Since, the host zeolite was different in these experiments, Figs. 7 and 8 report the activity of 5 wt.% MoO_3/ZSM-5, prepared via ammonium heptamolybdate impregnation and a catalyst prepared via phosphomolybdic acid impregnation to yield the same MoO_3 loading. It is quite apparent that, overall, the presence of phosphorus has a deleterious effect on performance. In other studies, which have employed impregnation from phosphoric acid solution, the addition of phosphate has been observed to poison the reaction [23], whereas those in which phosphorus was a zeolite framework species have reported promotion [24,25]. In the present study, it is quite likely that the dispersion of the molybdenum containing phase is influenced by the impregnation method, since in one case $Mo_7O_{24}{}^{6-}$ ions are being impregnated and in the other $[PMo_{12}O_{40}]^{3-}$. Within the literature, highly dispersed Mo precursor species, such as $Mo_2O_5{}^{2+}$ formed via migration of external MoO_3 entities [26], have been proposed as precursors to the most active species. The relative magnitude is large when consideration is given to the relative amount of phosphorus doped (which is in a 1:12 P:Mo atomic ratio, as dictated by the formula of the Keggin unit). This aspect has been further investigated and, as will be shown elsewhere [27], the addition of high levels of phosphorus to MoO_3/ZSM-5 catalysts suppresses the formation of benzene but not hydrogen. This observation is particularly interesting since methane cracking is a potential route to CO-free H_2 [1].

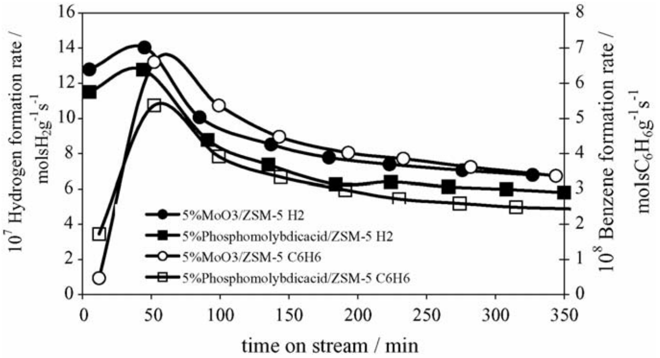

Fig. 8. Benzene and hydrogen formation rates as a function of time on stream for 5 wt.% MoO_3/Zeolist ZSM-5 and 5 wt.% MoO_3/Zeolist ZSM-5 prepared from phosphomolybdic acid (P/Mo atomic ratio = 0.08).

4. Conclusion

In this study, the effect of a number of dopants on the activity of MoO_3/ZSM-5 dehydroaromatisation catalysts has been investigated. Following previous literature, Co and Fe based dopants have been investigated. Contrary to previous observations, the addition of cobalt has not been observed to produce any pronounced promotional effect, other than an initial short-lived burst of activity. The origin of this discrepancy is currently not clear. However, promotional effects were observed with the use of iron dopants at longer times on stream, although these do not relate to coke suppression as previously reported. The use of novel Al containing dopants, leads to an enhancement of benzene formation rate. However, although the effect of Al is general, poor reproducibility has been observed with these catalysts and this is currently under investigation. Gallium doping also has a promotional effect, with a small increase in conversion being observed and a decrease in the relative ratio of hydrogen to benzene producing reactions. A pronounced supression of carbon laydown was evidenced with this catalyst. The co-impregnation of phosphorus via impregnation from a phosphomolybdic acid precursor leads to catalysts of reduced activity. It is possible to advance a number of possible reasons for the observed promotional/poisoning effects with dopants. However, since molybdenum/dopant phases are so highly dispersed they are difficult to characterise. It is anticipated that the use of EXAFS will prove informative in this respect. However, as a general feature, with the exception of phosphomolybdic acid impregnation, doping from acidic precursor solutions has a positive effect of benzene formation. This effect could be related to acidity modification, dealumination or re-dispersion of MoO_3 phases. The short burst of activity, observed in the case of the cobalt containing catalyst, is similar to profiles seen during the reduction/carbiding of other divalent metal containing compounds. It is possible that similar bursts of activity occur for the other catalysts, but they have consistently not been observed.

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