Study of W/HZSM-5-based catalysts for dehydro-aromatization of CH_4 in absence of O_2.
II. Action of promoters Zn and Li [*]

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By correlating the results of the NH_3-TPD characteristic study and the catalyst activity assay of the W/HZSM-5-based catalysts, we confirmed that the intensity and concentration of the surface B-acid sites have pronounced effects on the catalyst performance for dehydro-aromatization of methane (DHAM). It was found experimentally that, by addition of a proper amount of Mg^{2+}, the strong B-acid sites at the catalyst surface could be effectively eliminated, whereas the addition of a proper amount of Zn^{2+} or Li^{+} resulted not only in eliminating most of the strong surface B-acid sites but also in generating a kind of new medium-strong acid sites, mostly B-acid sites, simultaneously. The latter could serve as the catalytically active sites for dehydro-aromatization of methane; on such medium-strong surface B-acid sites, the formation of coke would be also alleviated to a greater extent. By simultaneous addition of Mg^{2+} and Zn^{2+}, optimized adjustment in surface acidity of the catalyst could be realized. On the other hand, the doping of the Zn^{2+} or Li^{+} component to the tungsten oxide matrix would facilitate inhibiting aggregation of the W-containing active species and improving dispersion of the W component at the surface of the catalyst, thus leading to a pronounced decrease in the reduction temperature for the hard-to-be-reduced W^{6+} species and an increase in quantity of the reducible W^{6+} species at the reaction temperature for DHAM, as has been evidenced by the results of a H_2-TPR study on the reducibility of the Zn^{2+} (or La^{3+}, Li^{+}, Mn^{2+})-promoted W/HZSM-5 system. The above two roles that Zn^{2+} and Li^{+} as promoters played both contributed to the persistence of high methane conversion and benzene selectivity, and the alleviation of coke deposition, as well as the prolongation of the catalyst lifetime.

KEY WORDS: methane; dehydro-aromatization; W–Zn (or Li)/HZSM-5; promoting action of Zn or Li; surface acidity; reducibility; NH_3-TPD; H_2-TPR

1. Introduction

The dehydro-aromatization of methane in the absence of O_2 (DHAM) has recently attracted considerable attention [1–9]. Tungsten-loaded HZSM-5 zeolite is among the most promising catalysts for the DHAM reaction [10]. Recent investigations in our laboratory have shown that, following an initial induction period, a methane conversion of *ca.* 20% could be achieved at a benzene selectivity of *ca.* 58% at 1073 K [11]. Similar to the Mo/HZSM-5-based catalysts, coke formation on the surface of functioning W/HZSM-5 catalyst is inevitable, which causes a gradual decline in methane conversion to benzene with time on stream. The results of evaluation of our W/HZSM-5 catalyst showed that, after 180 min of reaction, methane conversion and benzene selectivity both decreased to 12 and 35% from 20 and 58% as measured after the initial 60 min, respectively. Meanwhile, the molar fraction of carbon in the element composition of the catalyst surface increased to 75.0 mol% from 41.7 mol% as measured after the initial 60 min, indicating that a greater part of the surface of the functioning catalyst had been covered by coke. It has also been experimentally found that the catalytic performance of W/HZSM-5 for the DHAM reaction can be improved by addition of a proper amount of Zn, Li, Mn or La, as additives. Over a Zn-promoted catalyst 3% (percentage of mass, the same hereafter) W–1.5% Zn/HZSM-5 and under reaction conditions of 0.1 MPa, 1073 K, and GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}, methane conversion was increased by about 3% at almost the same benzene selectivity in the initial 180 min of reaction in comparison with those for non-promoted W/HZSM-5 catalyst. With the addition of Zn as promoter, not only is the DHAM activity of the catalyst significantly improved, but also the catalyst stability and lifetime are prolonged to a greater extent [11].

In the present work, effects of the additives, Zn, Li, Mg, La and Mn on the surface acidity and/or the reducibility of W/HZSM-5-based catalysts were investigated by using NH_3-TPD and H_2-TPR methods and correlating with the catalyst performance for the DHAM reaction. The results were used to elucidate the nature of promoting action by these additives.

2. Experimental

The W/HZSM-5 catalyst was prepared by the conventional incipient wetness method described previously [10,11].

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Zn (or Mg, Li, La, Mn)-promoted W/HZSM-5 catalyst was prepared by firstly impregnating a certain amount of the HZSM-5 zeolite carrier (with a Si/Al molar ratio of 38, obtained from the Chemical Plant of Nankai Univ., PR China) with a calculated amount of $ZnSO_4$ or $Mg(NO_3)_2$, Li_2SO_4, $La(NO_3)_3$, $MnSO_4$ (all of A.R. grade purity) in aqueous solutions, followed by drying at 393 K for 2 h, and then impregnating with a solution of NH_4OH, drying again at 393 K for 2 h and calcining at 673 K for 4 h, and subsequently impregnating with a calculated amount of H_2SO_4-acidified $(NH_4)_2WO_4$ aqueous solution ($pH = 2$–3), and finally drying at 393 K for 2 h and calcining at 773 K in air for 5 h. All the catalyst samples were pressed, crushed, and sieved to a size of 40–60 mesh.

The catalyst test for the DHAM reaction was conducted in a continuous flow tubular reactor–GC combination system and under reaction condition of 0.1 MPa, 1073 K, GHSV of feed-gas $CH_4 + 10\%$ Ar (as internal standard for GC analysis) at 960 h^{-1}. The reactant CH_4 and some small molecule carbon-containing products such as C_2H_6, C_2H_4 and CO, were alternatively determined by an on-line GC (model 103) equipped with dual thermal conductivity detectors (TCD) with a 5A zeolite molecular sieve column and a GDX-502 column separately, and aromatic hydrocarbon products were analyzed by another on-line GC (model 102GD) equipped with a thermal conductivity detector (TCD) and 2 m long dinonyl-phthalate (DNP) column, both with hydrogen as carrier gas. With an internal standard analyzing method, X_{CH_4} and selectivities of hydrocarbon products were evaluated.

The ammonia temperature-programmed desorption (NH_3-TPD) test was carried out on conventional temperature-programmed experimental equipment with an Omnistar GSD 3000 MS analyzer. 100 mg of catalyst sample was used for each test. Prior to NH_3-TPD measurement, the catalyst sample was pre-treated in a purified helium stream at 773 K for 30 min, followed by cooling down to 373 K in the helium stream and then switching to gaseous ammonia for adsorption for 1 h, and subsequently flushing by the helium stream at flow-rate of 50 ml/min for 1 h, and finally cooling down to room temperature. The NH_3-TPD test was conducted in the temperature region of 298–873 K with helium as carrier gas at a flow rate of 30 ml/min. The rate for temperature increase was 15 K/min.

Hydrogen temperature-programmed reduction (H_2-TPR) of the catalyst precursor was conducted on a fixed-bed continuous flow reactor–GC combination system. A KOH column and a 3A-zeolite molecular sieve column were installed in sequence at the reactor-exit to remove water vapor and H_2S formed by the reduction of metallic oxides and sulfates components of the catalyst sample. 50 mg of catalyst sample was used for each test. Prior to the H_2-TPR test, the sample was flushed by a purified argon stream, first at 673 K for 30 min to clean the surface of the catalyst sample, and then cooled down to room temperature, followed by switching to a N_2-carried 5 vol% H_2 gaseous mixture as reducing gas for starting the TPR test. Temperature increased at 15 K/min, with the highest reduction temperature being 1123 K. The change of hydrogen signal was monitored by using an on-line GC (model 102GD) with a thermal conductivity detector (TCD).

3. Results and discussion

3.1. NH_3-TPD study of surface acidity of the catalysts

NH_3-TPD spectra of the catalyst provided useful information about intensity and concentration of surface acid sites of the catalysts. Figure 1 shows the NH_3-TPD spectra of the W/HZSM-5 and the Mg^{2+}-doped W/HZSM-5 systems with different Mg^{2+}-doping amounts. For the 3% W/HZSM-5, the NH_3-TPD peaks appeared at ~535 and ~785 K, which may be ascribed to the desorption of two kinds of ammonia species adsorbed on weak acid (mostly L-acid) sites and strong acid (mostly B-acid) sites, respectively. The modification of Mg^{2+} to 3% W/HZSM-5 led to the decrease of intensity of the high-temperature (785 K) peak and a small downshift of its position. It can be also seen from figure 1 that the elimination of surface acid sites caused by the doping of Mg^{2+} first started at the strongest sites. With increasing Mg^{2+}-doping amount, the peak-temperature and area of the high-temperature peak gradually decreased, suggesting that intensity and concentration of surface B-acid sites of the catalyst were gradually declining. When the Mg^{2+}-doping amount increased to 0.3%, the high-temperature peak disappeared, indicating that most of the surface B-acid sites were lost.

Figure 2 shows the results of activity evaluation of a series of Mg-free or Mg-doped 3% W/HZSM-5 catalysts for the DHAM reaction. It is evident that, with parts of the strong acid sites eliminated by addition of a certain amount

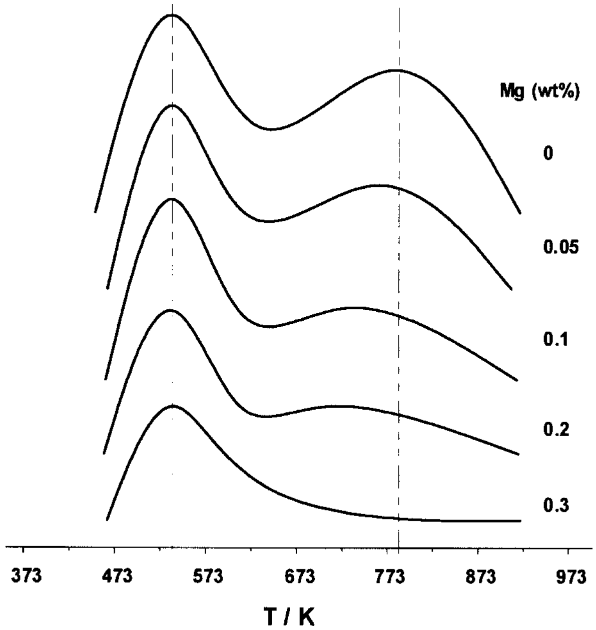

Figure 1. NH_3-TPD spectra of the Mg^{2+}-doped 3% W/HZSM-5 systems with different Mg^{2+}-doping amounts.

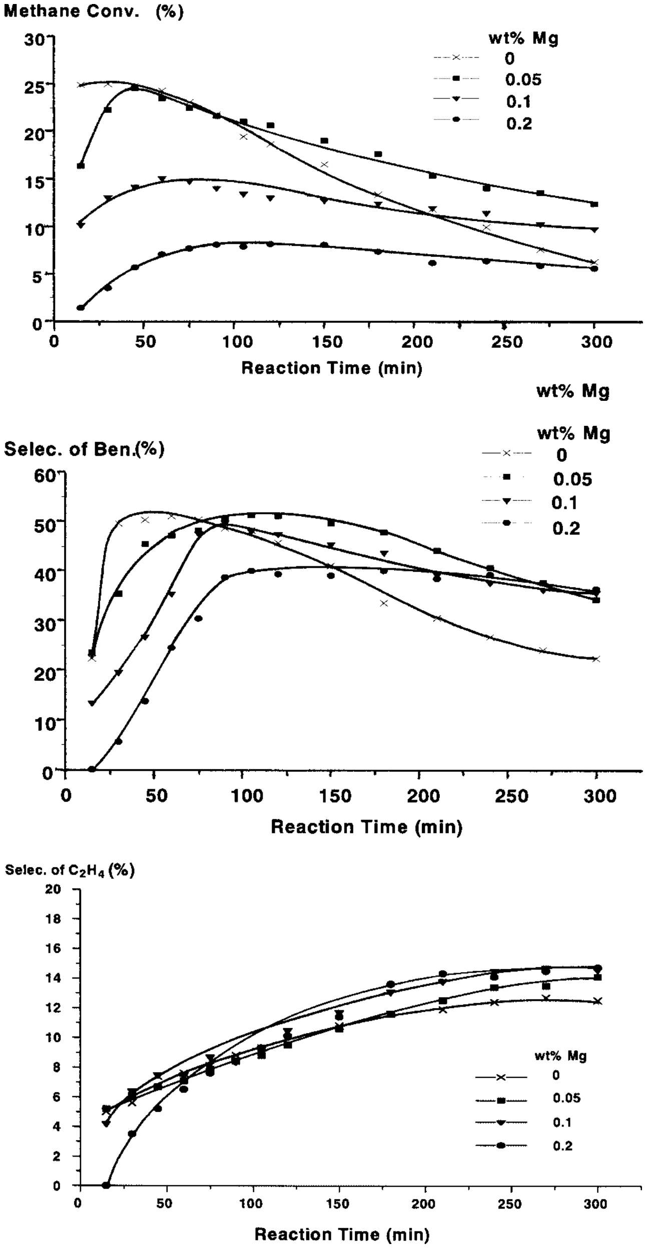

Figure 2. Results of activity assay of the Mg^{2+}-doped 3% W/HZSM-5 catalysts with different Mg^{2+}-doping amounts for DHAM. Reaction conditions: 0.1 MPa, 1073 K, GHSV = 960 h^{-1}.

of Mg^{2+} ions, the rate of initiation of the reaction decreased distinctively and the initial methane conversion was considerably declined. But the decline in methane conversion and benzene selectivity was relatively mild and the deactivation of catalyst was alleviated. The gradually enhanced ethylene selectivity probably implied that the decrease in concentration of the surface B-acid sites led to the decrease of rate of follow-up aromatiztion of the intermediate ethylene. Since deep dehydro-aromatization of methane on the strong B-acid sites was avoided, the coke formation was weakened to a certain extent, thus prolonging the lifetime of the catalyst.

The above results indicate that the intensity and concentration of surface B-acid sites of the W/HZSM-5-based catalysts have pronounced effects on their catalytic activity. Strong surface B-acid sites were expected to be in favor of the quick initiation of the reaction and the following aromatization of the intermediate ethylene. They also tended to promote the formation of coke, which blocked the zeolite pores and thus led to deactivation of the catalyst. On the other hand, although over-elimination of the surface B-acid sites would certainly be favorable to inhibiting or lightening coke formation thus prolonging the lifetime of the catalyst, it would inevitably lead to slowing down the initiation of the reaction and decreasing benzene selectivity. The intermediate ethylene may have not enough time to follow-up aromatization, and also be dehydrogenated to carbon deposits or polymerized to coke, resulting in the surface active sites of the catalyst being covered and the deactivation of the catalyst. It is thus clear that there exists an optimal degree for adjustment of the intensity and concentration of surface acid sites.

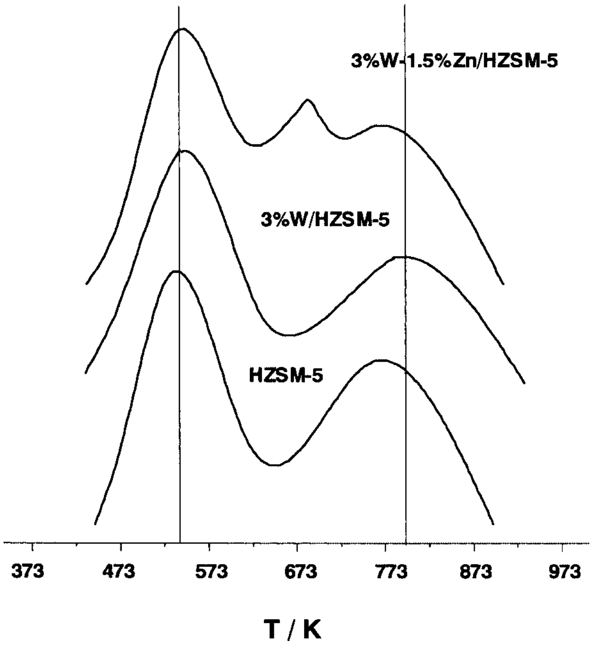

Figure 3. NH_3-TPD spectra of the 3% W–1.5% Zn/HZSM-5 and the related systems.

Figure 3 shows the NH_3-TPD spectra of the 1.5% Zn^{2+}-doped 3% W/HZSM-5 catalyst and related systems. Unlike the Mg^{2+}-doped systems, the modification of Zn^{2+} to W/HZSM-5 led to a decline of the intensity of the ~785 K peak on the one hand, and the emergence of a new peak at ~680 K on the other hand. It is obvious that the doping of Zn^{2+} resulted in the loss of a considerable amount of strong surface B-acid sites (as indicated by the NH_3-TPD peak at ~785 K), and in the mean time, generation of a type of new medium-strong surface acid sites, mostly B-acid sites, as indicated by the NH_3-TPD peak at ~680 K. This type of new medium-strong acid sites was expected to be able to serve as the catalytically active sites for dehydro-aromatization of methane. In order to gain further insight into the nature of such a type of new medium-strong surface acid sites, a

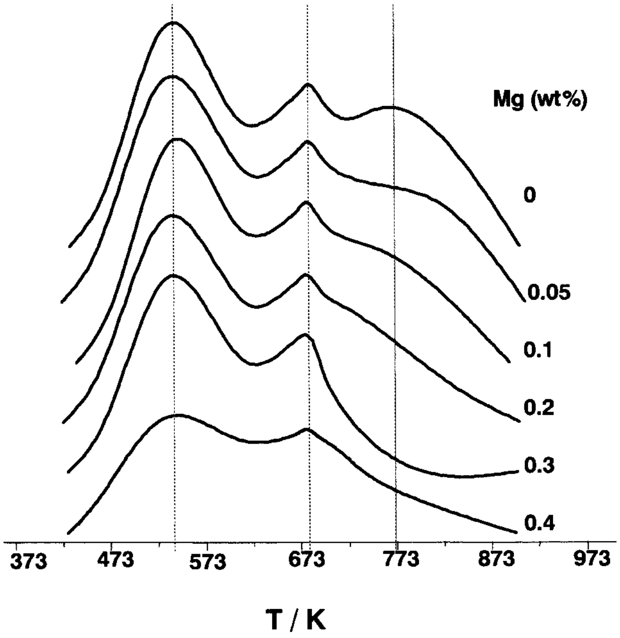

Figure 4. NH_3-TPD spectra of the Mg^{2+}-doped 3% W–1.5% Zn/HZSM-5 systems with different Mg^{2+}-doping amounts.

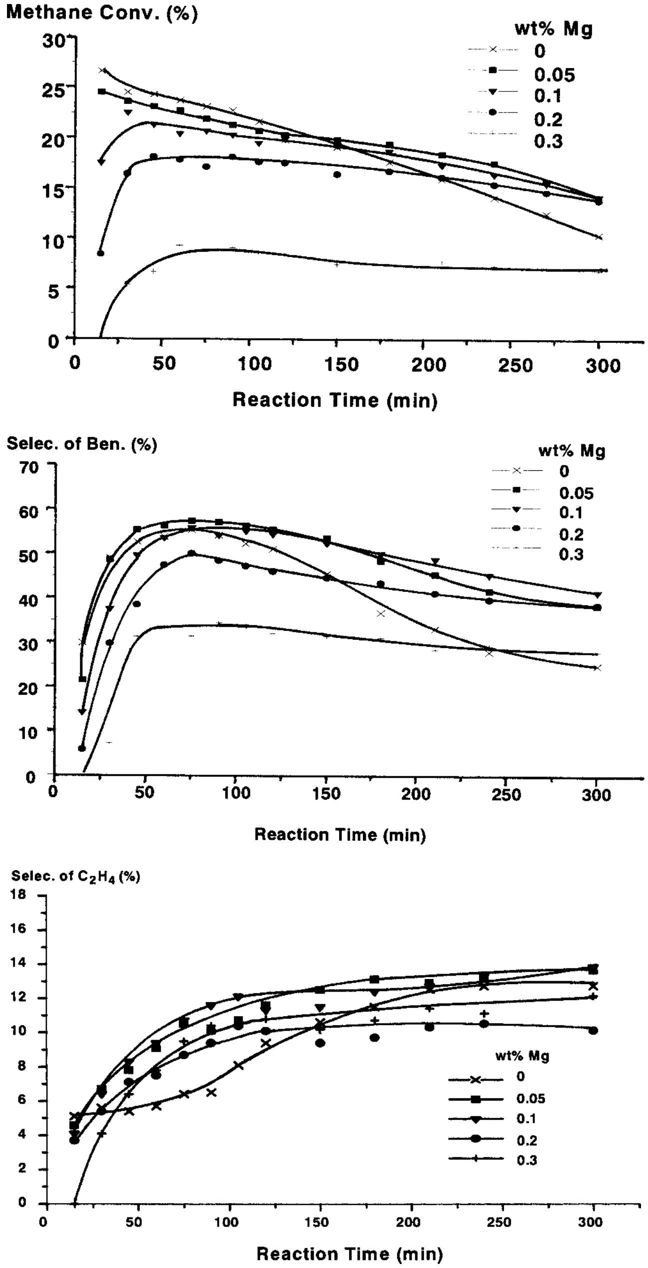

Figure 5. Results of activity assay of the Mg^{2+}-doped 3% W–1.5% Zn/HZSM-5 catalysts with different Mg^{2+}-doping amounts for DHAM. Reaction conditions: 0.1 MPa, 1073 K, GHSV = 960 h^{-1}.

characterization study of the surface acid sites by solid state proton-NMR method is indeed desirable.

Simultaneous incorporation of Mg^{2+} and Zn^{2+} into the W/HZSM-5 host catalyst would be expected to eliminate those strong surface B-acid sites and generate the new medium-strong acid sites more efficiently. Such results are illustrated in figure 4. It can be seen that the addition of Mg^{2+} of 0.2% was enough to eliminate almost all the strong B-acid sites, whereas the addition of Mg^{2+} of 0.4% led to further loss of some medium-strong and weak acid sites. It appears that the Mg^{2+}-doping of 0.1% was the optimal amount for 3% W–1.5% Zn/HZSM-5.

The results of activity assay of a series of Mg^{2+}-doped 3% W–1.5% Zn/HZSM-5 catalysts with different Mg^{2+}-doping amounts for DHAM are illustrated in figure 5. It is shown that, with addition of proper amounts of Zn^{2+} and Mg^{2+}, the performance of the catalyst for the DHAM reaction improved significantly. Over a 3% W–1.5% Zn–0.1% Mg/HZSM-5 catalyst, methane conversion reached 21–15% with the corresponding benzene selectivity at 55–42% during the initial 5 h of reaction (see table 1). The lifetime of the catalyst was thus prolonged to a great extent.

Li^+ is also found to be a good reagent to adjust the surface acidity of the catalyst. Modification of W/HZSM-5 by a proper amount of Li^+ was able to eliminate a large portion of strong surface B-acid sites of the catalyst (more specifically, of HZSM-5 zeolite support), simultaneously generating a considerable amount of a type of new medium-strong acid sites, as evidenced by the NH_3-TPD spectrum shown in figure 6. The results of activity assay of the catalyst (see figure 7) demonstrated that, over a 3% W–1.5% Li/HZSM-5 catalyst after an inductive period of approximately 1 h, methane conversion of 21% and benzene selectivity of 61.5% can be obtained. After 6 h of reaction, methane conversion and benzene selectivity still maintained at 17 and 50%, respectively (see table 1). Besides, doping of the Li^+ seemed to have little effect on the initiation rate of the catalytic reaction. The lifetime of catalyst was thus greatly prolonged.

Therefore, the above NH_3-TPD investigation, combined with the results of catalyst evaluation, clearly indicated that the intensity and concentration of the surface B-acid sites have a pronounced effect on the activity of catalytic dehydrogenation of methane. The stronger the surface acid sites, the lower the temperature for reaction initiation and the faster the reaction initiation. This meant that the higher the

Table 1
DHAM reaction activity over the catalyst systems with different promoters.[a]

Catalyst	Conversion of CH_4 (%)		Selectivity (%)			
			Ben.		C_2H_4	
	105th min	300th min	105th min	300th min	105th min	300th min
3% W/HZSM-5	19.5	6.2	48.2	22.0	9.2	12.4
3% W–0.05% Mg/HZSM-5	21.0	12.5	51.5	34.0	9.0	14.0
3% W–1.5% Zn/HZSM-5	21.5	11.0	52.0	25.0	8.0	12.8
3% W–0.1% Mg–1.5% Zn/HZSM-5	21.0	15.0	55.0	42.0	12.0	13.5
3% W–1.5% Li/HZSM-5	21.0	17.0	61.5	50.0	9.0	12.5

[a] The activity data of each catalyst taken at the 105th min and the 300th min of the reaction, respectively, under reaction conditions: 0.1 MPa, 1073 K, GHSV of feed-gas $CH_4 + 10\%$ Ar at 960 h^{-1}.

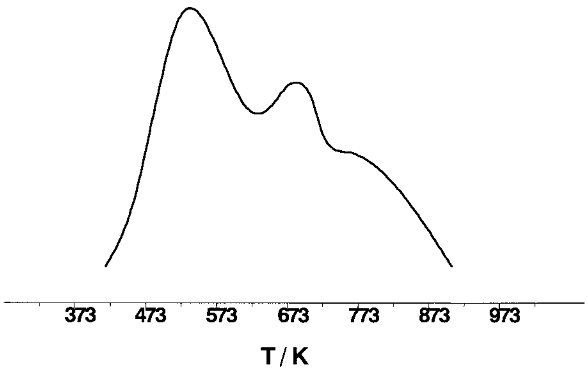

Figure 6. NH_3-TPD spectrum of the 3% W–1.5% Li/HZSM-5 catalyst.

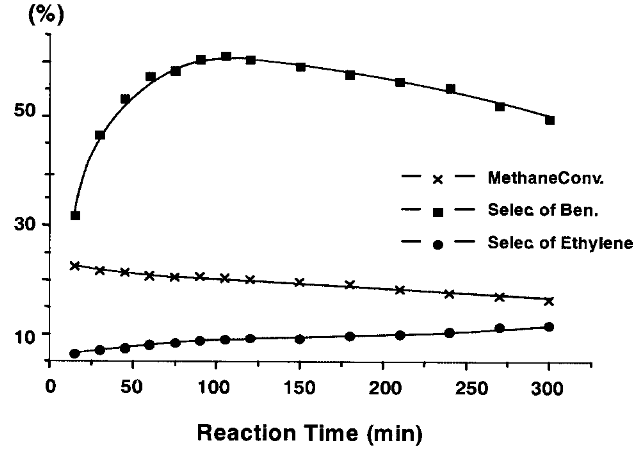

Figure 7. Results of activity assay of the 3% W–1.5% Li/HZSM-5 catalyst for DHAM. Reaction conditions: 0.1 MPa, 1073 K, GHSV = 960 h^{-1}.

dehydrogenation activity of methane, the heavier the coke, and thus, the shorter the catalyst lifetime. On the other hand, too weak a surface acidity was not good for gaining decent methane conversion, especially benzene selectivity. One of the roles that Zn^{2+}/Mg^{2+} or Li^{+} as promoter played was to eliminate most of the strong surface B-acid sites (thus reduce coke formation), and to generate a large amount of new medium-strong surface B-acid sites simultaneously, thus realizing optimized adjustment in surface acidity of the catalyst.

3.2. H_2-TPR characterization of reducibility of the catalysts

H_2-TPR of the catalyst provided useful information about the reducibility of catalyst. Figure 8 shows the H_2-TPR spectra taken on the W/HZSM-5-based catalyst precursors and the related system Zn/HZSM-5. For the W/HZSM-5 host catalyst, the observed H_2-TPR peaks that could be distinctively resolved were those at 819, 891 and 1073 K (see figure 8(a)). The two low-temperature reduction peaks (819 and 891 K) can be, respectively, ascribed to the two subsequent steps of single-electron reduction of the W^{6+} species derived from the $(WO_6)^{n-}$ precursor with octahedral coordination, $W^{6+} + e^- \rightarrow W^{5+}$ and $W^{5+} + e^- \rightarrow W^{4+}$, whereas the high temperature reduction peak (1073 K) was due to the single-electron reduction of the W^{6+} species derived from the $(WO_4)^{2-}$ precursor with tetrahedral coordination, $W^{6+} + e^- \rightarrow W^{5+}$, as demonstrated previously [10]. Doping of Zn^{2+} led to downshift of those TPR peaks (especially the 1073 K peak) and a large increase of their peak-area (especially of the low-temperature peaks at 819 and 891 K) (see figure 8 (b) *vs.* (a)).

Figure 8(c) shows the H_2-TPR spectrum of a 1.5% Zn/HSM-5 sample as reference taken at the same H_2-TPR experiment conditions. In view of the fact that the Zn component in the oxidation precursor of Zn/HZSM-5 existed in its sulfate form, *i.e.*, $ZnSO_4$, and it could be decomposed by H_2 reduction under the condition of H_2-TPR, *i.e.*, $ZnSO_4 + 4H_2 \rightarrow ZnO + H_2S + 3H_2O$ (which was analogous to the cases of H_2-reduced decomposition of $MgSO_4$ [12] and of catalytic reduction of SO_3 [13]), the observed reduction peak at 773 K in figure 8(c) may be ascribed to such a reduction process. Thus, the big and broad low-temperature peak centered at 819 K observed on the 3% W–1.5% Zn/HZSM-5 system (see figure 8(b)) should include the contribution from the reduction–decomposition of the Zn-sulfate component, in addition to that of reduction of the W component. By computer fitting and analysis, this big and broad low-temperature peak could be resolved to three subpeaks at 773, 819 and 871 K, among which the subpeak at 773 K could be assigned to the reduction–decomposition of the Zn-sulfate component, and the subpeak at 819 K most likely corresponded to the single-electron reduction of the W^{6+} species derived from the $(WO_6)^{n-}$ precursor,

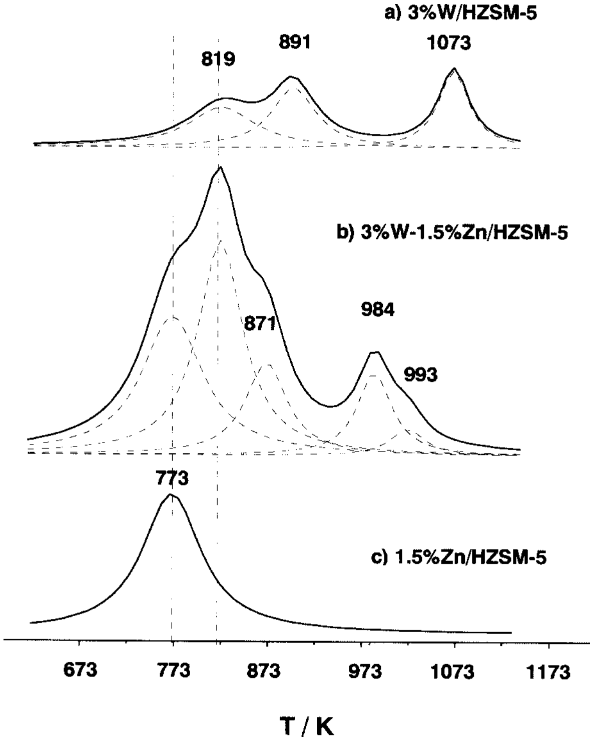

Figure 8. H_2-TPR spectra of the 3% W–1.5% Zn/HZSM-5 catalyst and the related systems.

$W^{6+} + e^- \rightarrow W^{5+}$. A large portion of the produced W^{5+} can be subsequently reduced to W^{4+}, with a corresponding reduction peak at 871 K. It is worth noting that the peak-temperature for the latter step of reduction was downshifted by ~20 K (*i.e.*, from 891 down to 871 K) due to the doping of the Zn^{2+}.

The doping of the Zn^{2+} also resulted in the high-temperature peak downshifting to 984 K from 1073 K (see figure 8 (a) *vs.* (b)). Following similar analysis as previously, this peak can be resolved to a main peak at 984 K and a shoulder peak at 993 K, which may be, respectively, attributed to the two steps of single-electron reduction of the W^{6+} species derived from the $(WO_4)^{2-}$ precursor with tetrahedral coordination, $W^{6+} + e^- \rightarrow W^{5+}$ and $W^{5+} + e^- \rightarrow W^{4+}$. Compared with that of the Zn-free system W/HZSM-5, the reduction of this kind of W^{6+} species became relatively easy due to the doping of the Zn^{2+}. The peak temperature for their first step of reduction was downshifted by ~89 K (*i.e.*, from 1073 to 984 K), and moreover, a portion of them could be further reduced to W^{4+}, with a corresponding shoulder peak at 993 K.

Assuming that the quantity of the reductively decomposed Zn-sulfate component in the 3% W–1.5% Zn/HZSM-5 system was equivalent to that of the 1.5% Zn/HZSM-5, through computer-fitting and comparison of area of the observed H_2-TPR peaks for the above three systems, it can be estimated that the areas of the H_2-TPD peaks at 819 and 871 K in figure 8(b) were 3.8 and 1.7 times as much as those at 819 and 891 K in figure 8(a). This indicates that the quantities of the $(WO_6)^{n-}$-derived W^{6+} species reducible to W^{5+} and W^{4+} in the 3% W–1.5% Zn/HZSM-5 were enhanced by 280 and 70% with doping of the Zn^{2+}, respectively, compared with those of the 3% W/HZSM-5. By similar analysis, the quantity of the $(WO_4)^{2-}$-derived W^{6+} species reducible to W^{5+} in the 3% W–1.5% Zn/HZSM-5 was 1.24 times as much as that of the 3% W/HZSM-5 (*i.e.*, the 984 K peak in figure 8(b) *vs.* the 1073 K peak in figure 8(a)), and 32% of them may be further reduced to W^{4+}. Conceivably, such remarkable enhancement of reducibility of the W component would certainly be in great favor of the improvement of the catalyst performance.

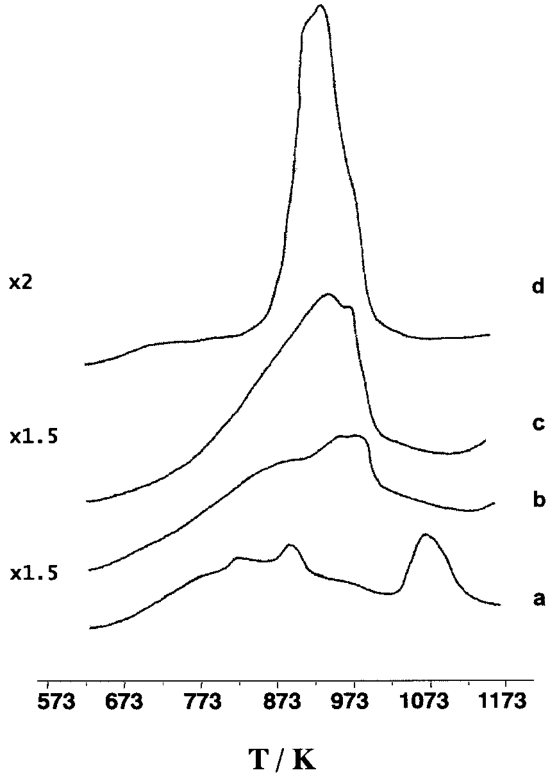

Figure 9. H_2-TPR spectra of the catalyst of: (a) 3% W/HZSM-5, (b) 3% W–1.5% La/HZSM-5, (c) 3% W–1.5% Li/HZSM-5 and (d) 3% W–0.5% Mn/HZSM-5.

Figure 9 (b), (c) and (d) shows the H_2-TPR spectra of the W/HZSM-5 systems doped by La^{3+}, Li^+, Mn^{2+}, respectively. Since La^{3+} and Li^+ both are non-reducible under the condition of H_2-TPR, the observed H_2-TPR peaks at 873–993 K should be due to the reduction of W^{n+} species. Mn^{2+} also has the behavior similar to that of La^{3+} and Li^+, although the observed strong H_2-TPR peak centered at 923 K included probably the contribution from the reduction of a minor amount of the Mn species with higher valence (which was probably produced in the process of calcination of the catalyst precursor at 673–773 K in air), in addition to that of reduction of the W component. It was clear that the La^{3+}- or Li^+- or Mn^{2+}-doping resulted not only in an increment in area of the H_2-TPR peaks ascribed to reduction of the W component of their corresponding systems, but also in a marked downshift of the position of the high-temperature peak (1073 K), leading to its partial overlapping with the corresponding low-temperature peak. This result seems to imply that the difference between the W^{6+} species derived from the $(WO_6)^{n-}$ precursors with octahedral coordination and those derived from the $(WO_4)^{2-}$ precursors with tetrahedral coordination became relatively ambiguous, probably due to the dispersion caused by the doped La^{3+} or Li^{+} or Mn^{2+}. As a result, the proportion of the reducible W^{6+} species in the total W amount at the temperatures $\leqslant$1000 K increased remarkably, which would facilitate decreasing the temperature needed for the reduction activation of the W/HZSM-5-based catalysts and enhancing the catalyst activity for DHAM reaction.

4. Conclusions

The experimental results confirmed that both Zn^{2+} and Li^{+} could serve as an efficient promoter for the W/HZSM-5 catalyst. The improvement of the activity and stability of the catalyst by the addition of the Zn^{2+} or Li^{+} promoter probably originated from the following factors:

(1) The doping of the Zn^{2+} or Li^{+} resulted in eliminating a large portion of strong surface B-acid sites which tend to lead to coke formation, and generating a lot of new medium-strong surface acid sites simultaneously. The latter could serve as the catalytically active sites for dehydro-aromatization of methane and could inhibit or alleviate formation of coke to a great extent.

(2) The doping of Zn^{2+} or Li^{+} component to the tungsten oxide matrix would facilitate improving dispersion of the W^{n+} component at the surface of catalyst, thus result in a pronounced decrease of the reduction temperature for the W^{6+} species, which are difficult to be reduced, and a large increase of the proportion of the reducible W^{6+} species in the total W amount at the reaction temperature for DHAM.

All these factors contributed to persistence of high methane conversion and benzene selectivity and prolongation of the catalyst lifetime.

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