Nonoxidative dehydrogenation and aromatization of methane over W/HZSM-5-based catalysts [*]

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Highly active and heat-resisting W/HZSM-5-based catalysts for nonoxidative dehydro-aromatization of methane (DHAM) have been developed and studied. It was found from the experiments that the W–H_2SO_4/HZSM-5 catalyst prepared from a H_2SO_4-acidified solution of ammonium tungstate (with a pH value at 2–3) displayed rather high DHAM activity at 973–1023 K, whereas the W/HZSM-5 catalyst prepared from an alkaline or neutral solution of $(NH_4)_2WO_4$ showed very little DHAM activity at the same temperatures. Laser Raman spectra provided evidence for existence of $(WO_6)^{n-}$ groups constructing polytungstate ions in the acidified solution of ammonium tungstate. The H_2-TPR results showed that the reduction of precursor of the 3% W–H_2SO_4/HZSM-5 catalyst may occur at temperatures below 900 K, producing W species with mixed valence states, W^{5+} and W^{4+}, whereas the reduction of the 3% W/HZSM-5 occurred mainly at temperatures above 1023 K, producing only one type of dominant W species, W^{5+}. The results seem to imply that the observed high DHAM activity on the W–H_2SO_4/HZSM-5 catalyst was closely correlated with $(WO_6)^{n-}$ groups with octahedral coordination as the precursor of catalytically active species. Incorporation of Zn (or La) into the W–H_2SO_4/HZSM-5 catalyst has been found to pronouncedly improve the activity and stability of the catalyst for DHAM reaction. Over a 2.5% W–1.5% Zn–H_2SO_4/HZSM-5 catalyst and under reaction conditions of 1123 K, 0.1 MPa, and GHSV = 1500 ml/(h g-cat.), methane conversion (X_{CH_4}) reached 23% with the selectivity to benzene at ~96% and an amount of coke for 3 h of operation at 0.02% of the catalyst weight used.

Keywords: methane, dehydro-aromatization, W/HZSM-5, W–H_2SO_4/HZSM-5, W–Zn (or La)–H_2SO_4/HZSM-5, polytungstates, promoting effect of Zn or La

1. Introduction

With the development of a series of new catalysts, nonoxidative dehydrogenation and aromatization of methane (DHAM) to aromatic hydrocarbons has drawn much attention in recent years [1–12]. This process has definite advantages, namely the less complicated technology and easy separation of the aromatic hydrocarbon products (benzene, toluene, etc.) from unconverted methane and the by-product hydrogen, which is a very valuable source of hydrogen for petroleum refining industry.

Bragin et al. [1] earlier reported 78% selectivity of benzene formation at 18% conversion of methane at 1023 K over a Pt–CrO_3/HZSM-5 catalyst in a pulse reactor. Since then, a few studies have been published on DHAM reaction over Mo/HZSM-5 [3,4], MoO_3/ZSM-5 or MoO_3/SiO_2 [5,6], Mo_2C/ZSM-5 [6,7], Mo–W/HZSM-5 [8], Mo–Pt/HZSM-5 [9], Mo–Ru/HZSM-5 [10], and Mo–Co (or Fe)/HZSM-5 [11]. Our previous work [12] showed that benzene was formed from methane over a Mo–Zn–H_2SO_4/HZSM-5 catalyst with average conversion of methane of 19% for 12 h and selectivity to benzene of ~90% at 1018 K (which are slightly higher than the values estimated from thermodynamics due to disregarding part of methane converted to coke in the calculations of methane conversion and selectivity to benzene).

Most of the existing catalysts for DHAM reaction so far are operating at about 973 K, so that the methane conversion achieved is low due to the thermodynamic limitation. Thermodynamic calculations carried out by us indicate that equilibrium conversions of 11.3, 16, 21, 27 and 33% for methane to benzene (i.e., $6CH_4 \rightleftharpoons C_6H_6 + 9H_2$) are predicted at 973, 1023, 1073, 1123 and 1173 K, respectively. This means that the operation temperature as high as ~1073 K is required for methane conversion of ~20% practically. However, under such high temperature, Mo-based catalysts suffer from the disadvantage of serious deactivation by fouling by coke formed in the process of DHAM and by losing of Mo component by sublimation [12]. Therefore, development of DHAM catalysts with high activity and stability at higher temperatures has potential significance for commercial utilization of DHAM process.

In the present work, highly active and heat-resisting W–H_2SO_4/HZSM-5-based catalysts were developed and studied. Incorporation of Zn (or La) into the W–H_2SO_4/HZSM-5 catalyst was found to markedly improve the DHAM activity and stability of the catalyst operating under relatively high temperatures.

2. Experimental

The catalysts were prepared by the method of incipient wetness, with the HZSM-5 zeolite with a Si/Al molar

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ratio of 38 (obtained from the Chemical Plant of Nankai University) as a carrier. A certain amount of the HZSM-5 zeolite was impregnated with ammonium tungstate aqueous solution containing a calculated amount of W, which was prepared by dissolving $(NH_4)_2WO_4$ (in A.R. grade of purity) in de-ionized water and adding a little of H_2SO_4 to regulate the pH value of the solution to 2–3, followed by drying at 383 K for 2 h, and then calcining at 773 K for 4 h; thus, a precursor of the W–H_2SO_4/HZSM-5 catalyst was obtained. The precursor of the W–Zn–H_2SO_4/HZSM-5 catalyst was prepared by impregnating the precursor of the W–H_2SO_4/HZSM-5 catalyst with aqueous solution of $ZnSO_4$ (in A.R. grade of purity), followed by drying at 383 K for 2 h, and then impregnating with a solution of NH_4OH, drying again at 383 K for 2 h, and finally calcining at 673 K for 4 h. With $(NH_4)_2MoO_4$ replacing $(NH_4)_2WO_4$, with $La(NO_3)_3$ replacing $ZnSO_4$, and an aqueous solution of $(NH_4)_2SO_4$ replacing the solution of NH_4OH, according to the same procedure of preparation as that for W–Zn–H_2SO_4/HZSM-5, the precursors of the Mo–Zn–H_2SO_4/HZSM-5 and the W–La–H_2SO_4/HZSM-5 catalysts were prepared, respectively. All these catalyst samples were pressed, crushed, and sieved to size of 40–60 mesh.

The evaluation experiment of catalyst activity was performed in a fixed-bed continuous-flow reactor–GC combination system operating under atmospheric pressure. The DHAM reaction over the catalysts was carried out at a stationary state and under the following reaction conditions: 1023–1173 K, and feed gas (CH_4) hourly-space velocity (GHSV) of 1500 ml/(h g-cat.). 0.6 g of catalyst sample was used each time for testing. Feed gas methane was in 99.9% purity. The reactant and products were analyzed by an on-line 102GD GC equipped with a hydrogen flame ionization detector and a thermal conductivity detector and 2 m long dinonyl phthalate (DNP) column, with nitrogen or hydrogen as carrier gas. The data were taken all at 60 min after the reaction starting, unless otherwise noted. Methane conversion ($X_{\mathrm{CH_4}}$) and product selectivity (S_{product}) were calculated upon the carbon number basis, with part of methane converted to coke neglected.

Raman spectra of the precursor solutions of tungstate to be supported were taken at room temperature by using a Spex Ramalog-6 laser Raman spectrometer, with the 514.5 nm line from a Spectra Physics model 164 argon ion laser used as the excitation source. Slit width settings correspond to a resolution of 4 cm^{-1}.

Temperature-programmed reduction (TPR) of catalyst in precursor (oxidation) state was conducted on a fixed-bed continuous-flow reactor–GC combination system. A N_2-carried 5 vol% H_2 gaseous mixture was used as reducing gas; the rate of elevating temperature was 10 K/min; 50 mg of catalyst was used each time for testing.

3. Results and discussion

3.1. Performance of catalyst for DHAM

The activity of W/HZSM-5 and Mo/HZSM-5 (as a contrast) catalysts modified by Zn–H_2SO_4 for DHAM reaction was evaluated at 1073 K, respectively. The results are illustrated in figure 1. It can be seen that the 2% (percentage of mass, the same below) W–1.5% Zn–H_2SO_4/HZSM-5 catalyst displays rather high activity and stability for DHAM reaction in comparison with the 2% Mo–1.5% Zn–H_2SO_4/HZSM-5 catalyst. Under reaction conditions of 1073 K, 0.1 MPa, and GHSV = 1500 ml/(h g-cat.), $X_{\mathrm{CH_4}}$ reached stably 20.5%, and the total amount of coke for 3 h was 0.02% of the catalyst weight used. In addition to benzene and toluene, trace C_{8+} aromatic hydrocarbons, including ethylbenzene, dimethylbenzene and naphthalene, can be found in the products (see sample #6 in table 1). Whereas over the Mo–Zn–H_2SO_4/HZSM-5 catalyst (sample #11 in table 1) and under the same conditions of reaction, $X_{\mathrm{CH_4}}$ reduced gradually from 19% at the first hour down to 13% after 3 h of DHAM operation, predicting that deactivation of the catalyst had occurred to a certain extent, very likely due to fouling by coke formed in the reaction process (a total amount of coke for 3 h equal to 0.5% of the catalyst weight detected) and losing of Mo component by sublimation (a pale-yellow deposit of Mo component on the inner wall of exit tube of the reactor observed).

Figure 2 showed the effect of amount of W loading on DHAM performance of the W-based catalyst. It can be seen that both $X_{\mathrm{CH_4}}$ and $S_{\mathrm{ben.}}$ increased initially with increasing amounts of W loading, and tended toward stable levels at W loading of 3.5%. It seems that an amount of W loading no less than 2.5% would be appropriate for the HZSM-5 carrier.

Figure 3 illustrates the effect of temperature on $X_{\mathrm{CH_4}}$ and $S_{\mathrm{ben.}}$ over the 2.5% W–1.5% Zn–H_2SO_4/HZSM-5 catalyst for DHAM reaction. $X_{\mathrm{CH_4}}$ increased with elevating temperature from 10.7% at 973 K up to 20.2% at 1073 K and reached 23.2% at 1173 K, and the $S_{\mathrm{ben.}}$ in this region

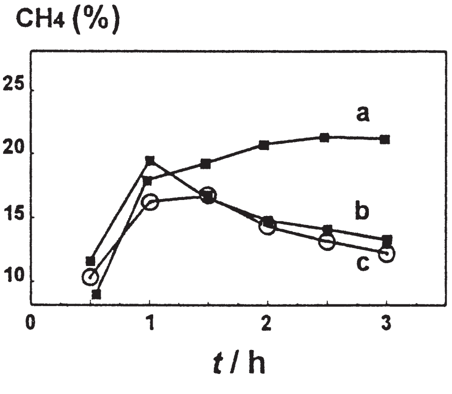

Figure 1. Stability testing of the catalyst of: (a) 2% W–1.5% Zn–H_2SO_4/HZSM-5; (b) 2% Mo–1.5% Zn–H_2SO_4/HZSM-5; (c) 2% W–H_2SO_4/HZSM-5. Reaction conditions: 1073 K, 0.1 MPa, GHSV = 1500 ml/(h g-cat.).

Table 1
The results of activity assays of the catalysts with different compositions for dehydro-aromatization of methane.[a]

Sample No.	Catalyst	T (K)	X_{CH_4} (%)	Selectivity[b] (%) C_2	C_3	Ben.	Tol.	C_8
1	HZSM-5	973	0.1	88.2	–	11.8	–	–
2	H_2SO_4/HZSM-5	973	0	–	–	–	–	–
3	Zn/HZSM-5	973	1.0	19.6	1.3	69.9	9.2	–
4	2.0% W/HZSM-5 (pH[c] = 7–9)	1023	0	–	–	–	–	
		1073	5.7	–	–	94.3	4.7	∼1
5	2.0% W–H_2SO_4/HZSM-5 (pH = 2–3)	1023	7.1	–	–	94.2	4.8	∼1
		1073	16.7	–	–	94.7	4.3	∼1
		1123	21.4	–	–	95.5	3.5	∼1
6	2.0% W–1.5% Zn–H_2SO_4/HZSM-5 (pH = 2–3)	1073	20.5	–	–	96.0	3.0	∼1
7	2.5% W–1.5% Zn–H_2SO_4/HZSM-5 (pH = 2–3)	973	10.7	–	–	92.3	6.7	∼1
		1073	20.2	–	–	94.2	4.8	∼1
		1123	23.0	–	–	96.7	2.3	∼1
		1173	23.2	–	–	97.0	2.0	∼1
8	2.5% W–1.5% La–H_2SO_4/HZSM-5 (pH = 2–3)	1123	22.3	–	–	94.6	4.4	∼1
9	4.0% Mo–H_2SO_4/HZSM-5	1023	12.5	–	–	91.8	7.2	∼1
10	4.0% Mo–1.0% Zn–H_2SO_4/HZSM-5	1023	15.8	–	–	92.6	6.4	∼1
11	2.0% Mo–1.5% Zn–H_2SO_4/HZSM-5	1073	19.0	–	–	93.8	5.2	∼1

[a] Reaction conditions: 0.1 MPa, GHSV = 1500 ml (CH_4)/(h g-cat.). All data were taken at 60 min after reaction starting.

[b] Trace C_{8+} aromatic hydrocarbons (ethylbenzene, dimethylbenzene, naphthalene, etc.) can be found in the products; the selectivity data listed here are slightly higher than realities due to disregarding part of methane converted to coke in the calculations of X_{CH_4} and selectivities.

[c] The pH value of the preparative solution of ammonium tungstate.

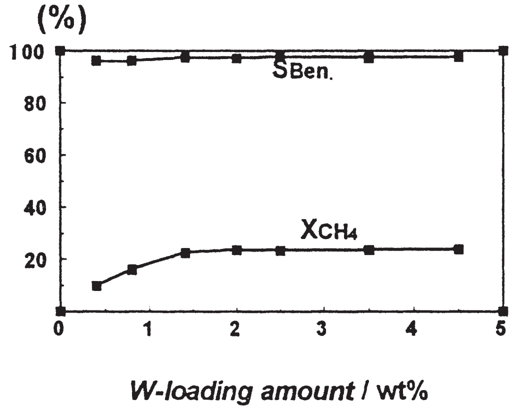

Figure 2. Effect of W loading in W–1.5% Zn–H_2SO_4/HZSM-5 on the catalyst performance. Reaction conditions: 1123 K, 0.1 MPa, GHSV = 1500 ml/(h g-cat.).

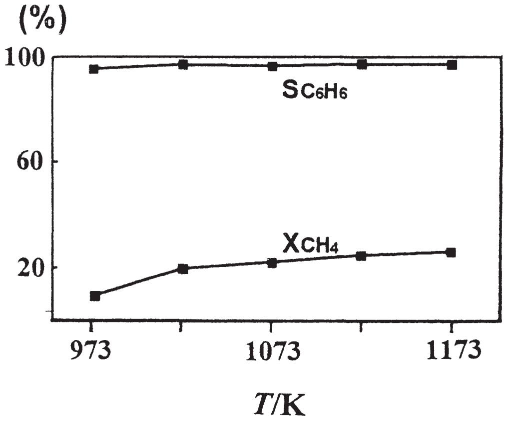

Figure 3. Effect of temperature on the performance of 2.5% W–1.5% Zn–H_2SO_4/HZSM-5 catalyst. Reaction conditions: 0.1 MPa, GHSV = 1500 ml/(h g-cat.).

of temperature is almost maintained at a level of about 95% (see sample #7 in table 1).

3.2. Effect of preparation condition on the catalyst activity

It has been found experimentally that selecting an appropriate pH value of the precursor solution of tungstate to be supported is one of crucial factors for preparation of highly active W/HZSM-5-based catalysts for DHAM. The result of a comparative testing demonstrated that a W/HZSM-5 catalyst prepared by impregnating the HZSM-5 carrier with the aqueous solution of ammonium tungstate with pH = 7–9, which was prepared by dissolving ammonium tungstate in de-ionized water or mixing tungstic acid and aqua ammonia, showed very little activity for DHAM reaction at the temperature of 973–1023 K, which is consistent with the result reported by Wang et al. [8]. Whereas over a W–H_2SO_4/HZSM-5 catalyst, prepared from a H_2SO_4-acidified aqueous solution of ammonium tungstate with the pH = 2–3, both X_{CH_4} and $S_{ben.}$ were dramatically enhanced (see table 1, sample #4 vs. sample #5). It could be inferred that the roles that addition of a small amount of H_2SO_4 plays were probably not only in enhancing the solubility of $(NH_4)_2WO_4$ in water so as to favor an increase in W loading amount in single-pass operation of impregnation, more importantly, also in resulting in formation of the polytungstates in the precursor solution via the reactions as follows:

$$6(WO_4)^{2-} + 7H^+ \rightleftharpoons (HW_6O_{21})^{5-} + 3H_2O$$

or/and

$$12(WO_4)^{2-} + 14H^+ \rightleftharpoons (H_2W_{12}O_{42})^{10-} + 6H_2O$$

Lowering the pH value of the precursor solution would shift the equilibria of the above reactions to the right. It has been known that these polytungstate ions are built of octahedral groups $(WO_6)^{n-}$ sharing edges, which is obviously different from $(WO_4)^{2-}$ ions with tetrahedral coordination [13]. The above result seems to imply that there may exist some correlation between the $(WO_6)^{n-}$ species with octahedral coordination derived from these polytungstate ions and the high DHAM activity of the catalyst.

Laser Raman spectra of the precursor solution provide further evidence for the existence of the polytungstate ions. In figure 4(a) is shown the Raman spectrum of an NH_4OH-alkalified solution of $(NH_4)_2WO_4$ with pH = 8–9, in which a Raman peak assignable to the symmetric stretching mode of tungstic radical ions WO_4^{2-} with tetrahedral coordination (T_d) was observed at 931 cm^{-1} [14]. For the neutral solution of $(NH_4)_2WO_4$ with pH = 7, as shown in figure 4(b), the peak at 931 cm^{-1} was obviously weakened, and simultaneously, a new peak appeared at 945 cm^{-1}, which may be due to the W=O stretching mode of tungstic acid molecules H_2WO_4 with C_{2v} symmetry. This means that tungstic radical ions coexisted with tungstic acid molecules:

$$2NH_4^+ + (WO_4)^{2-} + 2H_2O \rightleftharpoons 2NH_4OH + H_2WO_4$$

With pH value of the solution lowering to 2–3 by acidification of H_2SO_4, the peaks ascribed to discrete mono-tungstate species disappeared, and meanwhile, two new strong peaks at 983 and 971 cm^{-1} were observed (see figure 4(c)). The peak at 983 cm^{-1} is evidently due to the symmetric stretching mode of SO_4^{2-} ion with T_d symmetry [15]. The peak at 971 cm^{-1} may originate from the stretching vibration of terminal W=O of polytungstate species such as $(HW_6O_{21})^{5-}$ and $(H_2W_{12}O_{42})^{10-}$, which is quite analogous to the case of polymolybdates [16].

On the other hand, the results of H_2-TPR investigation showed that obvious difference in the reducibility existed between the two catalysts prepared from the two solutions of ammonium tungstates with different pH values, respectively. As shown in figure 5(a), the main H_2-TPR peak observed on the 3% W/HZSM-5 sample was present at 1073 K. In view of the result of EPR measurement carried out by us [17] that the H_2 reduction of this catalyst at 1073 K for 30 min produced only one type of W^{5+} species with a strong EPR signal ($g_{\parallel} = 1.82/g_{\perp} = 1.95$) and the intensity of this signal did not reduce with prolonging time for reduction (indicating that the further reduction of this type of W^{5+} species was quite difficult), the H_2-TPR peak at 1073 K may be mainly ascribed to single-electron reduction of the W^{6+} species derived from the $(WO_4)^{2-}$ ions, $W^{6+} + e^- \rightarrow W^{5+}$. On the 3% W–$H_2SO_4$/HZSM-5, the observed three distinct peaks were present at 819, 891 and 1073 K, respectively. The peak at 1073 K is quite similar to the peak at 1073 K for the W/HZSM-5 and, evidently, ascribable to the single-electron reduction of the same type of W^{6+} species derived from $(WO_4)^{2-}$ ions, whereas the peaks at 819 and 891 K are very probably due to the sequent two steps of single-electron reduction of another type of W^{6+} species, most probably derived from $(WO_6)^{n-}$ groups constructing polytungstate ions, $W^{6+} + e^- \rightarrow W^{5+}$ and $W^{5+} + e^- \rightarrow W^{4+}$. The area of the second peak is about 70% of that of the first one, implying that only about 70% of these W^{5+} species produced from the first step of reduction can be further reduced to W^{4+}. This is consistent with the results of our EPR observation [17], which showed that H_2 reduction of the W–H_2SO_4/HZSM-5 sample at 1073 K for 15 min produced two types of W^{5+} species with two strong EPR signals, corresponding to $g_{\parallel}^{(1)} = 1.82/g_{\perp}^{(1)} = 1.95$ and $g_{\parallel}^{(2)} = 1.88/g_{\perp}^{(2)} = 1.97$, respectively, and the intensity of the latter EPR signal was greatly reduced with the time for reduction prolonged to 60 min, implying that a considerable

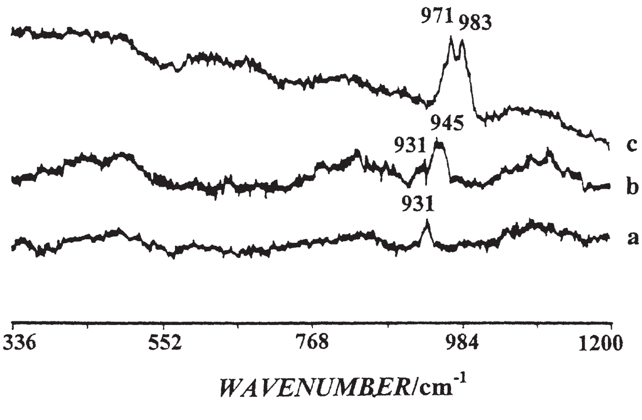

Figure 4. Raman spectra of the precursor solutions of: (a) $(NH_4)_2WO_4$ alkalified by NH_4OH with pH = 8–9; (b) $(NH_4)_2WO_4$ with pH = 7; (c) $(NH_4)_2WO_4$ acidified by H_2SO_4 with pH = 2–3.

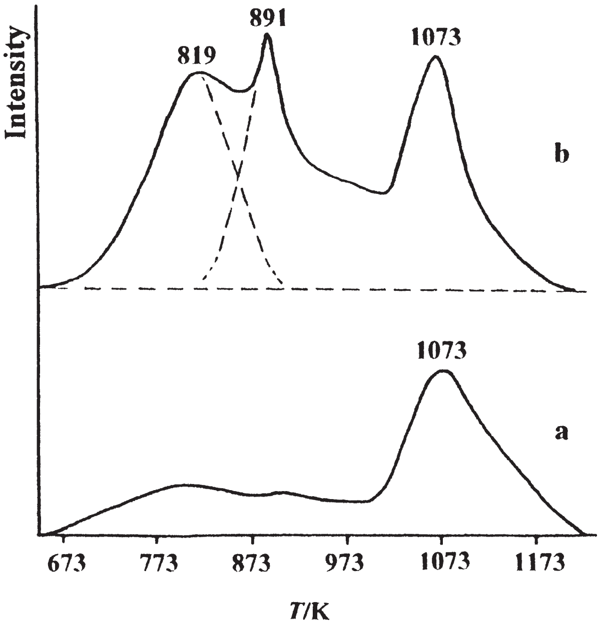

Figure 5. H_2-TPR spectra of the catalysts (in oxidation state) of: (a) 3% W/HZSM-5; (b) 3% W–H_2SO_4/HZSM-5.

proportion of the second type of W^{5+} species was further reduced to W^{4+} valence state of EPR silence.

Thus, it seems to us that, on the W–H_2SO_4/HZSM-5 catalyst, the observed high DHAM activity may originate from the pronounced reducibility of the supported W species in the catalyst precursor, of which a large proportion was derived from $(WO_6)^{n-}$ groups rather than $(WO_4)^{2-}$ ions; these W^{6+} species derived from $(WO_6)^{n-}$ groups may be reduced at relatively low temperature, and a considerable proportion of them may be reduced to the valence state of W^{4+} under the reaction conditions for DHAM.

3.3. The promoting effect of Zn, or La on DHAM activity of the W–H_2SO_4/HZSM-5 catalyst

It is experimentally found that the DHAM activity of W–H_2SO_4/HZSM-5 catalyst can be improved by addition of Zn, or La, as an additive. The results of activity assays of several catalysts with different compositions for dehydro-aromatization of methane are summarized in table 1. The HZSM-5 zeolite acidified by H_2SO_4 was completely inactive for methane conversion. The W–H_2SO_4/HZSM-5 (sample #5) catalyst prepared from a solution of ammonium tungstate acidified by H_2SO_4 displayed relatively high activity for the methane conversion, but deactivated gradually, as shown in figure 1(c). Whereas over a Zn-promoted catalyst, 2.5% W–1.5% Zn–H_2SO_4/HZSM-5 (sample #7), methane conversion was pronouncedly enhanced, reaching 23% with a selectivity of 96.7% to benzene under reaction conditions of 1123 K, 0.1 MPa, and GHSV $=$ 1500 ml/(h g-cat.).

Addition of a small amount of Zn to the Mo–H_2SO_4/HZSM-5 catalyst can also improve the performance of the catalyst for DHAM reaction to a certain extent, as evidenced by the result of the activity assay of samples #9 and #10 at 1023 K shown in table 1. However, the losing of Mo component by sublimation would inevitably lead to deactivation of the catalyst under the reaction temperature as high as 1073 K and above, as shown in figure 1(b).

Incorporating La as an additive was also found to significantly enhance DHAM activity of the W–H_2SO_4/HZSM-5 catalyst, but its promoting effect was somewhat not so remarkable as that of Zn. The experimental results also showed that, in order to gain the promoting effect as large as possible, an optimum match of W with the promoter, Zn or La, in their loading amounts was requisite.

By comparison of the methane conversions and the selectivities over the singly and doubly acid-promoted W/HZSM-5 catalysts, it is easy to find that, with the addition of Zn (or La) promoter, not only is the DHAM activity of the catalyst improved significantly, but the catalyst stability is also prolonged. As shown in figure 1, after 3 h of the operation, the Zn-promoted W–H_2SO_4/HZSM-5 catalyst (sample #6) maintained the methane conversion still at $\sim$20%, whereas the singly acid-promoted catalyst W–H_2SO_4/HZSM-5 (sample #5) deactivated gradually. It seems to us that the improvement of the activity and stability of the catalyst by addition of Zn (or La) promoter originates probably from the following factors: on the one hand, the presence of a Zn or La component in tungsten oxide matrix would be favorable to alleviate coke deposition and to inhibit aggregation of W-containing active species and formation of WO_3 crystallites at the surface of catalyst, and, on the other hand, the presence of a sulfate radical in the form of Zn (or La) sulfate would be in favor of stabilization of the B-acid sites by formation of hydrogen-sulfate radical (HSO_4^-) and, therefore, would tend to reduce, if not avoid, losing of B-acid at the surface of the catalyst. For better understanding of the mechanism of the promoter action, more works, especially more detailed knowledge about the nature of catalytically active sites, are needed.

4. Conclusions

(1) The W–H_2SO_4/HZSM-5 catalyst prepared by impregnating the HZSM-5 zeolite (Si/Al $=$ 38) carrier with an aqueous solution with pH $=$ 2–3 of ammonium tungstate acidified by H_2SO_4 has been demonstrated to be an highly effective catalyst for methane nonoxidative dehydro-aromatization. The high DHAM activity of the W–H_2SO_4/HZSM-5 catalyst for methane nonoxidative conversion seems to be closely associated with $(WO_6)^{n-}$ groups with octahedral coordination as the precursor of catalytically active species.

(2) The incorporation of Zn (or La) into the W–H_2SO_4/HZSM-5 catalyst is found to markedly enhance the activity and stability of the catalyst for methane nonoxidative dehydro-aromatization. The W–Zn–H_2SO_4/HZSM-5 catalyst is demonstrated to be a more promising catalyst for nonoxidative dehydro-aromatization of methane with its high activity and good performance of heat- and coking-resistance.

References

[1] O.V. Bragin, T.V. Vasina, A.V. Preobrazhenskii and K.M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim. (1982) 954; (1989) 750.

[2] T. Koerts, M.J.A.G. Deelen and R.A. van Santen, J. Catal. 138 (1992) 101.

[3] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.

[4] D.J. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.

[5] F. Solymosi, A. Erdohelyi and A. Szoke, Catal. Lett. 32 (1995) 43.

[6] F. Solymosi, J. Cserenyi, A. Szoke, T. Bansagi and A. Oszko, J. Catal. 165 (1997) 150.

[7] F. Solymosi, A. Szoke and J. Cserenyi, Catal. Lett. 39 (1996) 157.

[8] S. Wong, Y. Xu, L. Wang, S. Liu, G. Li, M. Xie and X. Guo, Catal. Lett. 38 (1996) 39.

[9] L. Chen, L. Lin, Z. Xu, T. Zhang and X. Li, Catal. Lett. 39 (1996) 169.

[10] Y. Shu, Y. Xu, S. Wang, L. Wang and X. Guo, J. Catal. 170 (1997) 11.

[11] S. Liu, Q. Dong, R. Ohnishi and M. Ichikawa, Chem. Commun. (1997) 1455.

[12] J.L. Zeng, Z.T. Xiong, G.D. Lin, H.B. Zhang and K.R. Tsai, in: 11th ICC, Baltimore, 1996, Po-158; J. Xiamen Univ. 35 (1996) 900.
[13] A.F. Well, *Structural Inorganic Chemistry*, 5th Ed. (Clarendon Press, Oxford, 1984) p. 519, and references therein.
[14] N. Weinstock, H. Schulze and A. Muller, J. Chem. Phys. 59 (1973) 5063.
[15] Landolt-Bornstein, *Physikalisch-Chemische Tabellen*, Vol. 2 (1951).
[16] H. Knozinger and H. Jeziorwski, J. Phys. Chem. 82 (1978) 2002; 83 (1979) 1166.
[17] J.L. Zeng, Z.T. Xiong, L.J. Yu, G.D. Lin and H.B. Zhang, J. Xiamen Univ. 37 (1998), in press.