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# Promotional Effect of Ru on the Dehydrogenation and Aromatization of Methane in the Absence of Oxygen over Mo/HZSM-5 Catalysts

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**A reaction rate of methane conversion of 14.54 nmol$^{-1}$ m$^{-2}$ and the formation rate of aromatics of 2.22 nmol$^{-1}$ m$^{-2}$ at 973 K for the dehydrogenation and aromatization of methane in the absence of oxygen was attained over Mo–Ru/HZSM-5 catalysts. By comparison, over unpromoted Mo/HZSM-5 catalysts, the reaction rate of methane conversion was 10.17 nmol$^{-1}$ m$^{-2}$ and the formation rate of aromatics was 1.52 nmol$^{-1}$ m$^{-2}$. The Ru-promoted Mo/HZSM-5 catalysts also show better stability. The catalyst with 2% Mo loading and with Mo/Ru atomic ratio ranging from 3 to 7 shows much better catalytic performance. $NH_3$-TPD shows that the addition of Ru onto 2Mo/HZSM-5 causes a further decrease in the amount of strong acid sites and at the same time, creates new acid sites with moderate acid strengths. TPR and DTA studies illustrate that the existence of Ru with a proper dispersion promotes the reduction of Mo species and the splitting of the C–H bond of methane.**

## 1. INTRODUCTION

Recently, methane dehydrogenation and aromatization in the absence of oxygen on Mo/HZSM-5 have received much attention (1–5). It is now well established that methane can be activated in the absence of oxygen on Mo/HZSM-5 catalyst with a conversion of about 6–8% and a selectivity to aromatics of about 90% at 973 K (only a carbon balance in the gas phase is considered). Solymosi *et al.* (3, 6, 7) and Lunsford *et al.* (5) gave more complete results by considering the total carbon or hydrogen balance in both gas and solid (carbon deposition) phases. They pointed out that methane can be activated in the absence of oxygen over Mo/HZSM-5 catalyst with a conversion of about 10–12% and a selectivity to aromatics of about 70–80% at 973 K. Further studies on this subject revealed that the acid sites and channel structure of HZSM-5 and the state and location of Mo species are crucial factors for good catalytic performance (1, 2, 8–14). Various techniques, such as specific surface area (BET), X-ray diffraction (XRD), $NH_3$ temperature-programmed desorption ($NH_3$-TPD), *in situ* X-ray photoelectron spectroscopy (XPS), differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FT-IR), $NH_4OH$ extraction, and $^{27}$Al and $^{29}$Si nuclear magnetic resonance (NMR) (13), etc., had been used to characterize the Mo/HZSM-5 catalysts. These results lead to a better understanding of the bifunctional nature of Mo/HZSM-5 catalysts and the nature of the interaction between Mo species and the HZSM-5 zeolite and, therefore, enhance our knowledge of the possible active Mo species and possible pathway of the reaction. On the basis of these studies a mechanism in which the reduction of Mo species by methane (1, 11), the polarization of a C–H bond of methane with the assistance of Mo species and the dehydrogenation of methane itself on Mo active sites, and the formation of ethylene as reaction intermediate which then undergoes oligomerization and aromatization on Mo modified Brønsted acid sites was suggested (2). Very recently, Solymosi *et al.* (6, 7) and Lunsford *et al.* (5) suggested that during the initial induction period the original $Mo^{6+}$ ions in the zeolite were reduced and carbided to $Mo_2C$ and methane activation occurred on $Mo_2C$ sites, leading to the formation of $C_2H_4$. After testing with $Mo_2C$ as catalyst for methane aromatization, Solymosi *et al.* further suggested that $Mo_2C$–$MoO_2$ with an oxygen deficiency may be the active sites for methane activation (6).

From the viewpoint of potential industrial application the methane conversion is too low. Two thermodynamic calculations for the reaction of methane to benzene showed that the limit of methane conversion at 973 K is 11.5%; therefore, there is still room for catalyst improvement. Several kinds of promoters had been tested to improve the catalytic performance of Mo/HZSM-5 catalysts. Wang *et al.* reported that introduction of W and Zr species can enhance the activity of Mo/HZSM-5 catalysts (8, 11, 14). Lately, the promotional effect of Pt on the reaction over Mo/HZSM-5 was studied (15). The authors claimed that the incorporation of Pt into Mo/HZSM-5 greatly enhances catalyst stability, but has no effect on the activity of the 2Mo/HZSM-5 catalyst.

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By comparing methane aromatization over Mo/HZSM-5 with the aromatization of short-chain paraffins over Zn/HZSM-5 and/or Ga/HZSM-5, it is interesting to note that there are many similarities. The former reaction can be recognized as a special example in which the polarization of one C–H bond in methane is more severe and, in fact, is an extension of the latter reaction. Lastly, Choudhary *et al.* (16) reported that methane can be highly activated and hence converted to higher hydrocarbons and aromatics with high conversion rates at low temperatures ($<$873 K), by a hydrogen transfer reactions with alkene over H–Galloaluminosilicate zeolite. With a mixture of methane and alkene and/or higher alkane, high rates of conversion to higher hydrocarbons and aromatics (about 10–45%) were possible. Usually, it is well recognized that Zn/HZSM-5 and Ga/HZSM-5 catalysts are bifunctional (dehydrogenating and acidic functions) (17, 18). For a catalyst to give good catalytic performances for the aromatization of short-chain paraffins, it is necessary to have a good and proper match between dehydrogenating and acidic properties. It seems reasonable to suppose that this principle is also applicable to methane aromatization over Mo/HZSM-5 catalysts. Since proper reduction and/or carbidation of Mo species is important for the reaction, Pt may be too active for dehydrogenation and hydrogenation and is not a suitable promoter for either short chain paraffins or methane aromatization (15, 17). We expect the addition of some transition metal which is less active for dehydrogenation and hydrogenation onto Mo/HZSM-5 will be beneficial to both catalytic activity and stability. Indeed, we found that Mo–Ru/HZSM-5 catalysts exhibit a reaction rate of methane conversion of 14.54 nmol$^{-1}$ m$^{-2}$ and the formation rate of aromatics of 2.22 nmol$^{-1}$ m$^{-2}$ at 973 K. By comparison, the reaction rate of methane conversion was 10.17 nmol$^{-1}$ m$^{-2}$ and the formation rate of aromatics was 1.52 nmol$^{-1}$ m$^{-2}$ over Mo/HZSM-5 catalysts. Furthermore, the catalyst shows much better stability compared to the unpromoted Mo/HZSM-5 catalyst. In this paper, we report the promotional effect of Ru transition metal on the catalytic performance of Mo/HZSM-5 catalyst. The possible function of Ru in Mo–Ru/HZSM-5 catalysts is discussed on the basis of catalyst characterization and catalytic studies.

## 2. EXPERIMENTAL

### 2.1. *Catalyst Preparation*

NaZSM-5 zeolite was supplied by Nankai University with a $SiO_2/Al_2O_3$ ratio of 50. The procedure of catalyst preparation was described in our previous papers (1, 2, 9). Briefly, NaZSM-5 zeolite was first converted into the ammonium form ($NH_4$ZSM-5) by repeated ion-exchange with a 1 *N* $NH_4NO_3$ aqueous solution at about 368 K, then dried at 383 K and calcined at 773 K for 6 h. 2Mo/HZSM-5 catalysts were prepared by impregnation with ammonium heptamolybdate (AHM) and then dried and calcined as before. Ru transition metal cations were introduced by impregnating 2Mo/HZSM-5 with an aqueous solution of the corresponding chloride and then dried at 383 K overnight and calcined. The samples were pressed, crushed, and sorted into sizes of 40–60 mesh. Usually, the notation used for the catalyst is 2Mo–*x*Ru/HZ, where *x* denotes the percentage of Ru transition metal loading and HZ is the abbreviation for HZSM-5. In some cases, in order to study the influence of the impregnation sequence, *x*Ru/HZ was first prepared and then *x*Ru–2Mo/HZ was prepared by the impregnation of *x*Ru/HZ with AHM.

### 2.2. *Catalyst Evaluation*

The catalytic test was performed in a fixed-bed continuous-flow 8-mm i.d. quartz reactor as described in our previous papers (1, 2, 9). Normally, the catalyst charge was 0.2 g. It was heated under an air stream (15 ml/min) to 873 K and maintained at 873 K for 30 min. After the pretreatment stage, methane was introduced into the reactor through a Brooks mass flow controller at a space velocity of 1500 ml $CH_4$ per gram of catalyst per hour. The pressure of the reactor system was 2 atm and the reaction temperature was 973 K in a standard test. The tail gas was sampled periodically and analyzed by a Shimadzu GC-9AM gas chromatograph equipped with a hydrogen flame ionization detector (FID). The reaction rate of methane conversion, and the formation rates of the higher hydrocarbons ($C_2^=$, $C_2^0$, and $C_3$) and benzene and toluene were calculated on the basis of a carbon number balance between the reactant entering and the products coming out of the reactor but without accounting for any coke formation. A sample was taken after 40 min on stream in a standard test. Methane was 99.95% pure. Analysis of the air and $N_2$ used in the experiment showed the absence of any $H_2$ and hydrocarbons.

### 2.3. *Catalyst Characterization*

Specific surface area and average pore diameter of the samples were obtained by the BET method at the liquid nitrogen temperature of 78 K, using a value of 0.162 nm$^2$ for the cross-sectional area of $N_2$. The measurement was performed with a Micromeritics ASAP-2000 equipment and data were processed and analyzed by an IBM computer.

XRD patterns were obtained on a Rigaku diffractometer using Cu $K\alpha$ radiation at room temperature with instrumental settings of 40 kV and 50 mA. Powder diffractograms of the samples were recorded over a range of $2\theta$ values from $5^\circ$ to $50^\circ$ at a scanning rate of $8^\circ$/min. All XRD patterns were recorded, stored, and processed by a computer system.

$NH_3$-TPD was performed on a conventional set-up equipped with a thermal conductivity detector (TCD). The catalyst charge was 0.14 g (particle size 40–60 mesh). It was first flushed with He (20 ml/min) at 873 K for 40 min and then cooled to 423 K and saturated with $NH_3$ until equilibrium. The sample was then flushed with He again until the integrator's baseline was stable. $NH_3$-TPD was then promptly started at a heating rate of 25 K/min from 423 to 873 K.

Temperature-programmed reduction (TPR) was carried out in a conventional flow apparatus. A sample of about 0.1 g was placed in a quartz reactor and flushed with $N_2$ and then heated in air at 873 K for 30 min. It was finally cooled to room temperature and was then reduced under a $H_2$ (5 vol%)–$N_2$ stream at a flow rate of 25 ml/min. The heating rate was 10 K/min from room temperature to 1083 K. TPR profiles recorded with pure $MoO_3$ and mechanical mixture of $MoO_3$ and HZSM-5 were also included for comparison.

Static CO chemisorption was performed in a glass adsorption system at room temperature to determine the dispersion of Ru in Mo–Ru/HZSM-5 catalysts with different Mo/Ru atomic ratios. The sample was reduced in flowing $H_2$ of 60 ml/min at 573 K for 2 h. It was cooled down to room temperature in a $H_2$ stream. Then the sample was evacuated in a vacuum system and heated up to 573 K. When the sample had cooled down to room temperature again, different pressures of CO were introduced into the sample tube and kept for 5 min for adsorption equilibrium. The procedure was repeated again. By supposing the stoichiometrical ratio of irreversible chemisorbed CO and surface Ru was 1, Ru dispersion on 2Mo–Ru/HZ catalysts can be calculated.

DTA profiles were recorded on a Perkin–Elmer DTA 1700 instrument as follows. The first profile was obtained by heating the sample from room temperature to 973 K at a heating rate of 10 K/min under a stream of $CH_4$ with a flow rate of 40 ml/min. After the sample was cooled to room temperature, a second profile was obtained by heating the sample up again to 973 K at a heating rate of 10 K/min under an air stream with a flow rate of 40 ml/min.

## 3. RESULTS AND DISCUSSION

### 3.1. *Effect of Ru Additive on the Catalytic Performance of 2Mo/HZ*

The addition of Ru transition metal cations onto 2Mo/HZ catalyst results in a better catalytic performance. It is interesting to note that the catalytic behavior of 2Mo–Ru/HZ catalysts is sensitive to the atomic ratio of Mo and Ru as summarized in Table 1. If a proper amount of Ru cation is introduced onto 2Mo/HZ so that on average every Ru atom is shared by 3 to 7 Mo atoms, the catalysts show their best catalytic performance. The effect of Ru on the catalyst with Mo/Ru atomic ratio higher than 7 or less than 3 is detrimental for the dehydrogenation and aromatization of methane. 2Mo–Ru/HZ catalysts with Mo/Ru atomic ratio ranging from 3 to 7 on average give the rate of methane conversion of about 14.54 $nmol^{-1}\ m^{-2}$ and the rate of aromatics formation of about 2.22 $nmol^{-1}\ m^{-2}$, in comparison with the rate of methane conversion of about 10.17 $nmol^{-1}\ m^{-2}$ and the rate of aromatics formation of about 1.52 $nmol^{-1}\ m^{-2}$ over 2Mo/HZ.

The introduction of Ru transition metal onto 2Mo/HZ catalyst also has a positive effect on its catalytic stability as we can see from Fig. 1 where the reaction rate of methane conversion is plotted vs time on stream. 2Mo/HZ catalyst shows a quick drop in activity while 2Mo–0.5Ru/HZ is much more stable. Figure 2 shows the dependence of the reaction rate of methane conversion and the formation rates of higher hydrocarbons and aromatics on time on stream. It appears that the stability of 2Mo–0.3Ru/HZ catalyst is still better than 2Mo/HZ, but not as good as 2Mo–0.5Ru/HZ as we can see from Figs. 1 and 2.

### 3.2. *Effect of Ru Additive on Physical Properties of 2Mo/HZ*

Table 2 summarizes the BET surface areas, pore volumes, and average pore diameters of Ru-promoted 2Mo/HZ catalysts. The physical properties of these samples are quite

**TABLE 1**

**Reaction Rate of Methane Conversion over 2Mo–Ru/HZ Catalysts with Different Mo/Ru Atomic Ratios**

| Catalysts | Mo/Ru atomic ratio | Reaction rate of $CH_4$ ($nmol^{-1}\ m^{-2}$) | Formation rate ($nmol^{-1}\ m^{-2}$) of | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $C_2^=$ | $C_2^0$ | $C_3$ | Benzene | Toluene | Aromatics |
| 2Mo/HZ | — | 10.17 | 0.26 | 0.21 | 0.01 | 1.42 | 0.10 | 1.52 |
| 2Mo–0.1Ru | 21.3 | 9.61 | 0.34 | 0.23 | 0.02 | 1.30 | 0.09 | 1.39 |
| 2Mo–0.3Ru | 7.0 | 14.94 | 0.29 | 0.25 | 0.01 | 2.11 | 0.17 | 2.28 |
| 2Mo–0.5Ru | 4.2 | 14.37 | 0.31 | 0.25 | 0.01 | 2.03 | 0.15 | 2.18 |
| 2Mo–0.7Ru | 3.0 | 14.42 | 0.27 | 0.25 | 0.01 | 2.07 | 0.14 | 2.21 |
| 2Mo–1.0Ru | 2.1 | 10.26 | 0.30 | 0.23 | 0.01 | 1.30 | 0.19 | 1.49 |

*Note.* Reaction temperature, 973 K; hourly space velocity of methane, 1500 $h^{-1}\ g^{-1}$.

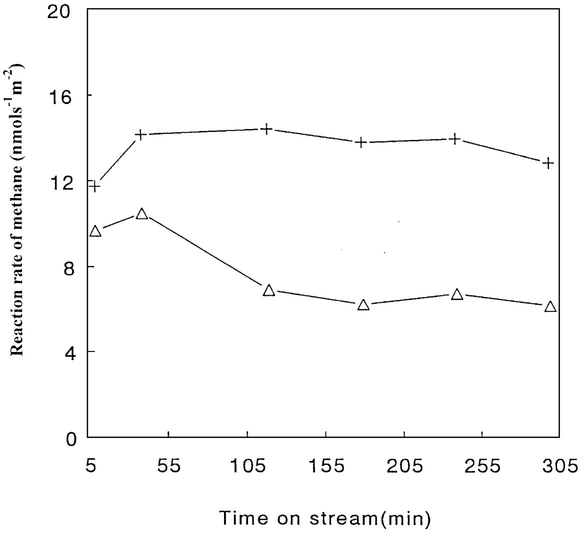


**FIG. 1.** Reaction rates of methane conversion over 2Mo–0.5Ru/HZ (+) and 2Mo/HZ (△) catalysts vs time on stream.

similar to the 2Mo/HZ catalyst. The XRD patterns of 2Mo–Ru/HZ catalysts with Ru contents ranging from 0.1 to 1% are also similar as we can see from Fig. 3. With these results, we may speculate that the different catalytic performances of various catalysts are mainly caused by the difference in chemical and not physical properties.

### 3.3. *Effect of Impregnation Sequence and Pretreatment on Catalytic Performance over 2Mo–Ru/HZ Catalysts*

Table 3 summarizes the effect of Ru additives on its dispersion. With increasing Ru loadings, Ru dispersion drops very fast and with 2Mo–1.0Ru/HZ catalyst it is not possible to measure any irreversible CO chemisorption. The impregnation sequence of Mo and Ru transition metal cations during the catalyst preparation is also of importance for good catalytic performance. If Ru is impregnated first, then the reaction rate of methane conversion and the formation rate of aromatics over 0.5Ru–2Mo/HZ catalyst will be less than on 2Mo/HZ catalyst although in this case the Ru dispersion is about 1. On the other hand, if 2Mo/HZ is first prepared and then modified by Ru cations, then 2Mo–0.5Ru/HZ catalyst will show a better catalytic performance as we can see from Fig. 4 but with a Ru dispersion of 0.5. This result implies that the location of Mo species on and/or in HZSM-5 zeolite is a crucial factor for the preparation of an active catalyst for the reaction and that in order to get a better promotional effect, a proper dispersion between 0.35 and 0.85 is desirable.

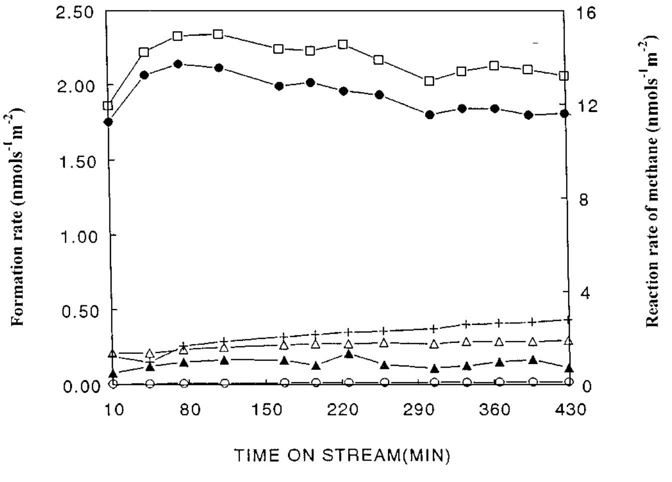


**FIG. 2.** Dependence of the reaction rate of methane conversion and the formation rate of various products on time on stream over 2Mo–0.3Ru/HZ catalyst. +, $C_2H_4$; △, $C_2H_6$; ○, $C_3H_8$; ●, $C_6H_6$; ▲, $C_7H_8$; □, $CH_4$.

**TABLE 2**

**BET Surface Area, Pore Volume, and Average Pore Diameter of Ru-Promoted 2Mo/HZ Catalysts**

| Samples | Surface area ($m^2$/g) | Micropore volume (cc/g) | Average pore diameter (nm) |
|---|---|---|---|
| 2Mo/Hz | 128 | 0.04 | 1.58 |
| 2Mo–0.1Ru | 122 | 0.04 | 1.57 |
| 2Mo–0.3Ru | 122 | 0.04 | 1.58 |
| 2Mo–0.5Ru | 123 | 0.04 | 1.57 |
| 2Mo–0.7Ru | 120 | 0.04 | 1.59 |
| 2Mo–1.0Ru | 125 | 0.04 | 1.57 |
| 0.5Ru–2Mo | 129 | 0.04 | 1.57 |

Since small $MoO_3$ crystallites are the precursors of active Mo species for the reaction as suggested in our previous papers (2, 12), it seems reasonable that the pretreatment temperature will have a strong influence on the catalytic performance, because the migration and aggregation of Mo species is strongly dependent on temperature. Figure 5 illustrates the influence of pretreatment temperatures on the

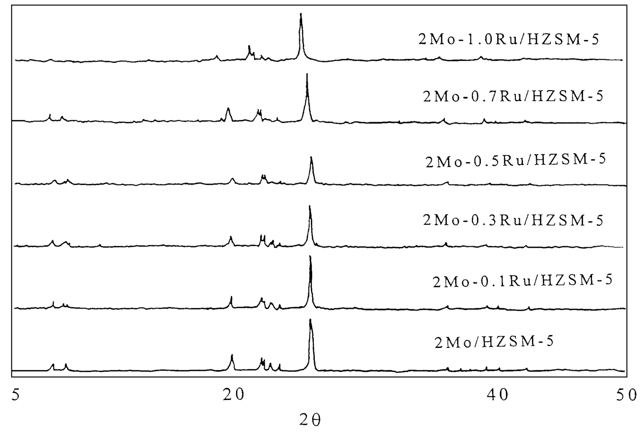


**FIG. 3.** XRD patterns of 2Mo–Ru/HZ catalysts with different Ru contents.

## TABLE 3

**Ru Dispersion of 2Mo–Ru/HZ Catalysts with Different Mo/Ru Atomic Ratios**

| Catalysts | Mo/Ru atomic ratio | Ru dispersion |
|---|---|---|
| 2Mo/HZ | — | 0 |
| 2Mo–0.3Ru | 7.0 | 0.84 |
| 2Mo–0.5Ru | 4.2 | 0.51 |
| 2Mo–0.7Ru | 3.0 | 0.36 |
| 2Mo–1.0Ru | 2.1 | ∼0 |
| 0.5Ru–2Mo | 4.2 | 1.0 |

*Note.* Assuming COirrev./Ru(surf.) = 1 at room temperature.

catalytic performance of 2Mo–0.5Ru/HZ catalyst. If the pretreatment temperature is too low to overcome the corresponding energy threshold, then the aggregation and migration of Mo and Ru species may be impossible. On the other hand, if the pretreatment temperature is too high, then the aggregation and migration of Mo and Ru species will be greatly accelerated and most of the Mo and Ru species will migrate into and aggregate to large $MoO_3$ crystallites and large Ru particles in the channel and, therefore, there are much less small $MoO_3$ crystallites and small Ru particles on the surface. Indeed, we found that 2Mo–0.5Ru/HZ catalyst pretreated in air at 873 K exhibits the best catalytic performance as shown in Fig. 5.

### 3.4. *Effect of Ru Additive on the Acidity of 2Mo/HZ*

Figure 6A shows the $NH_3$-TPD profiles of HZSM-5, 2Mo/HZ, and 2Mo–0.5Ru/HZ catalysts. Two peaks can be observed in the $NH_3$-TPD profiles of HZSM-5 zeolite. One is at 543 K (named as peak L) resulting from the desorption of $NH_3$ from weak acid sites and the other at 673 K (named as peak H) from strong acid sites. It seems clear that the introduction of Mo and Ru cations reduces the amount of strong acid sites. Figure 6B shows the $NH_3$-TPD profiles of Ru–Mo/HZ catalysts with different Mo/Ru ratio and the relative amounts of total acid sites of various 2Mo–Ru/HZ catalysts are listed in Table 4. Combining the results of Fig. 6 and Table 4, we can see that the amount of strong acid sites decreases with increasing Ru content in 2Mo–Ru/HZ catalysts whereas the amount of medium and weak acid sites increases if the Ru loading is less than or equal to 0.7%. However, the amount of strong acid sites increases again at a Ru loading of 1.0% as we can see from the corresponding profile in Fig. 6B. Usually the increased amount in medium and weak acid sites is less than the decreased amount in strong acid sites and therefore the relative amounts of total acid sites on most 2Mo–Ru/HZ catalysts are less than 1. Combining this result with that of the corresponding catalytic test (see Table 1), it seems that strong acid sites are not favorable for the dehydrogenation and aromatization of methane.

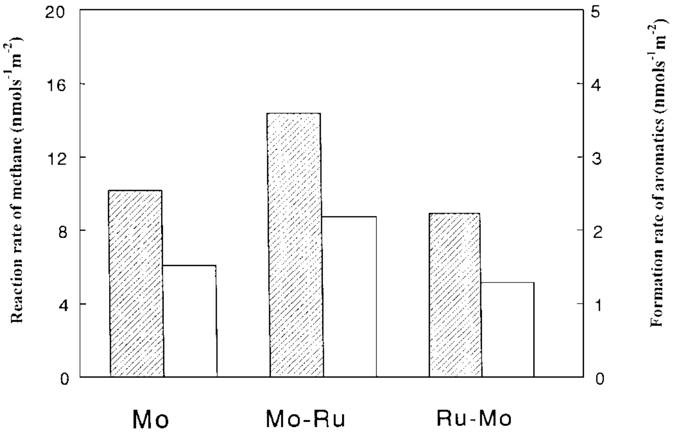


**FIG. 4.** The influence of impregnation sequence on the catalytic performance of Ru promoted 2Mo/HZ catalysts. ▨, reaction rate; □, formation rate of Ar.

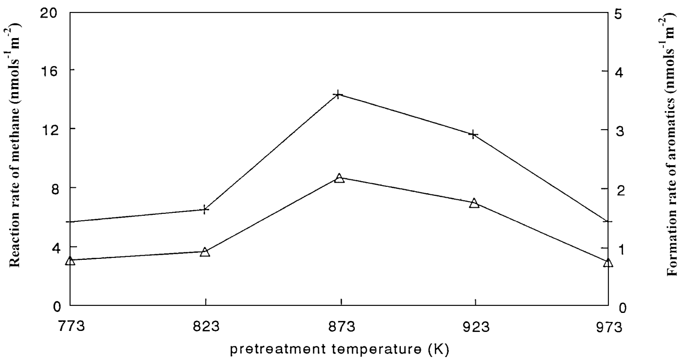


**FIG. 5.** Effect of pretreatment temperature on the reaction rate of methane conversion over 2Mo–0.5Ru/HZ catalyst. +, reaction rate; △, formation rate of Ar.

### 3.5. *The Effect of Ru Modification on the Reduction of Mo Species on 2Mo/HZ*

Figure 7A compares the TPR profiles of $MoO_3$, 2Mo/HZ catalyst, and a mechanical mixture of $MoO_3$ and HZSM-5

## TABLE 4

**Peak Temperatures of $NH_3$-TPD Spectra and the Relative Amount of Total Acid Sites on 2Mo–Ru/HZ Catalysts**

| | $NH_3$-desorption peak temperature | | |
|---|---|---|---|
| Catalyst | Peak L | Peak H | Relative amount of total acid sites |
| $NH_4$ZSM-5 | 523 | 723 | — |
| 2Mo/HZ | 523 | 723 | 1.0 |
| 2Mo–0.1Ru | 548 | | 0.83 |
| 2Mo–0.3Ru | 528 | | 0.85 |
| 2Mo–0.5Ru | 523 | | 0.91 |
| 2Mo–0.7Ru | 523 | | 0.74 |
| 2Mo–1.0Ru | 533(638) | | 0.99 |

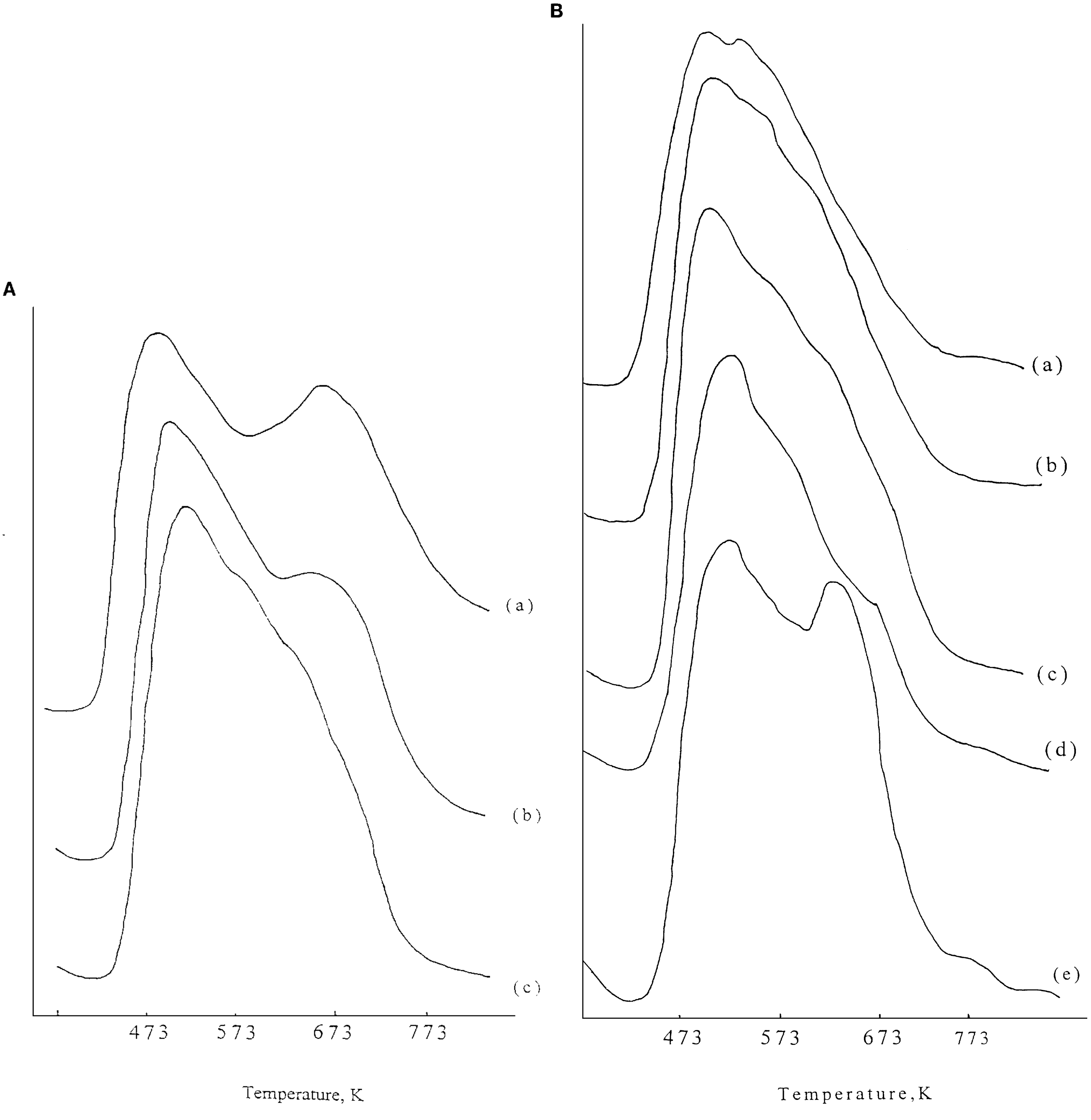


**FIG. 6.** (A) $NH_3$-TPD profiles of HZSM-5 (a), 2Mo/HZ (b), and 2Mo-0.5Ru/HZ (c). (B) $NH_3$-TPD profiles of 2Mo–Ru/HZ catalysts with different Ru contents. (a) 2Mo–0.1Ru/HZ; (b) 2Mo–0.3Ru/HZ; (c) 2Mo–0.5Ru/HZ; (d) 2Mo–0.7Ru/HZ; (e) 2Mo–1.0Ru/HZ.

with a Mo content of about 2%. Figure 7B shows the TPR profiles of 2Mo–Ru/HZ samples. The peak temperatures recorded during the experiments are listed in Table 5. Obviously, the first peak temperature (between 517–573 K) can be attributed to the reduction of Ru species. The corresponding area of this reduction peak increases with increasing Ru loading and the peak shifts to lower temperatures (from 573 to 517 K). This is a general trend as we usually observed a similar shift on other supported metal catalysts. The other two peaks may be attributed to the reduction of Mo species. It is noteworthy that there is an additional reduction peak at 805 K for the mechanical mixture of $MoO_3$ and HZSM-5 sample. Again, the highest TPR peak temperature (peak 3) shifts markedly to lower temperatures (from 1059 to 1003 K) with increasing amount of Ru. When the Ru loading is higher than 0.7%, this peak becomes a shoulder. The corresponding areas of the reduction peaks also decrease with increasing Ru loading as we can see from

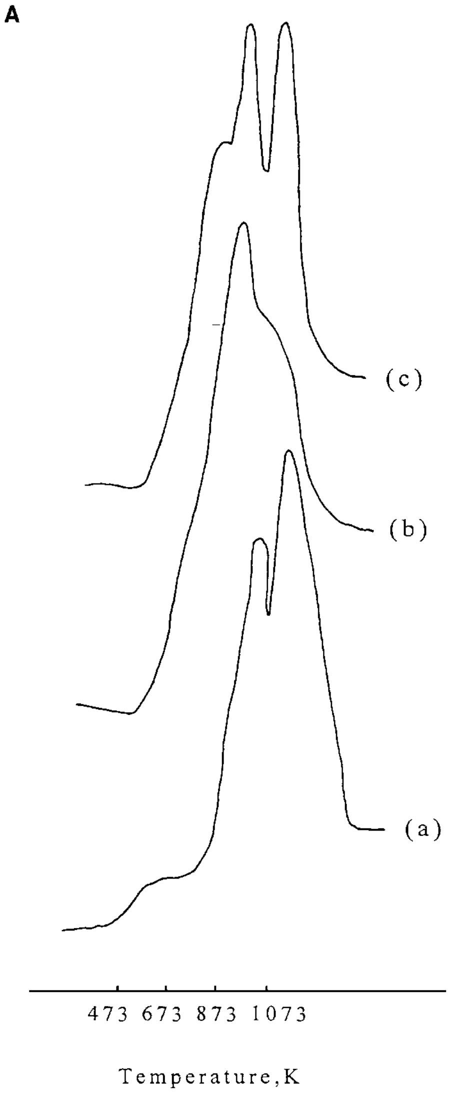


**FIG. 7.** (A) TPR profiles of $MoO_3$ (a), 2Mo/HZ (b) catalyst, and a mechanical mixture of $MoO_3$ and HZSM-5 (c). (B) TPR profiles of 2Mo–Ru/HZ catalysts with different Ru contents. (a) 2Mo–0.1Ru/HZ; (b) 2Mo–0.3Ru/HZ; (c) 2Mo–0.5Ru/HZ; (d) 2Mo–0.7Ru/HZ; (e) 2Mo–1.0Ru/HZ.

Fig. 7B. Meanwhile, the temperature of Peak 2 remains almost constant as summarized in Table 5. Although we could not get quantitative results for the TPR experiments at the moment (the trouble is probably due to a high temperature effect), the promotional effect of Ru on the reduction of Mo species is obvious. This conclusion is further supported by DTA experiments.

It is interesting that during the DTA experiments under a methane stream, we found an endothermic peak at a temperature of about 930 K. Figure 8A shows that with the 2Mo/HZ sample there is an endothermic peak at about 941 K, but at 927 K for the 2Mo–0.5Ru/HZ catalyst. Referring to our previous study by XRD, XPS, and a multichannel mass spectrometer (1, 11), we believe that this endothermic

**TABLE 5**

**Peak Temperatures of TPR Spectra from 2Mo–Ru/HZ Catalysts**

| Catalyst | TPR peak temperature (K) | | |
|---|---|---|---|
| | Peak 1 | Peak 2 | Peak 3 |
| $MoO_3$ | | 1029 | 1093 |
| $MoO_3$ + HZSM-5 (2% mixture) | | 925 | 1059 |
| 2Mo/HZ | | 899 | 1059 |
| 2Mo–0.1Ru | 573 | 893 | 1056 |
| 2Mo–0.3Ru | 557 | 891 | 993 |
| 2Mo–0.5Ru | 513 | 897 | 1003 |
| 2Mo–0.7Ru | 523 | 901 | |
| 2Mo–1.0Ru | 517 | 896 | |

peak reflects the splitting of one C–H bond of methane and the reduction of Mo species. No such endothermic peak was detected with HZSM-5 zeolite. This is evidence of the promotional effect of Ru species on the splitting of the C–H bond of methane and the reduction of Mo species. The reduction of Mo species is of importance as we pointed out in our previous paper (11).

A successive DTA experiment under an air stream supports the above suggestion. With 2Mo/HZ or 2Mo–0.5Ru/HZ catalyst there is an exothermic peak at about 673 K. This exothermic peak is due to the oxidation of carbonaceous species on the catalyst surface. Consistent with the results of DTA under a methane stream, no exothermic peak could be detected with the HZSM-5 sample. On the other hand, it is interesting to compare the results obtained from 2Mo/HZ and 2Mo–0.5Ru/HZ catalysts. The ratio of the amount of carbonaceous deposits on 2Mo–0.5Ru/HZ and on 2Mo/HZ is about 2.25 : 1. Combining these results with their catalytic tests, it appears that the more active 2Mo–0.5Ru/HZ catalyst produces much more carbonaceous species than the less active 2Mo/HZ catalyst. Furthermore, the exothermic peak temperature for 2Mo–05Ru/HZ catalyst is about 692.5 K, while it is 675 K for 2Mo/HZ catalyst. This implies that the more active and stable catalyst forms a more stable carbonaceous species on the catalyst surface. If the carbon deposition on the catalysts only plays a negative role for the reaction, the result seems unreasonable. A reasonable explanation is that the carbonaceous species formed during the reaction on the catalyst surface may play a positive role for the aromatization of methane. This is in agreement with the mechanism proposed by Solymosi *et al.* (6, 7) and Lunsford *et al.* (5). They suggested that during the initial induction period the original $Mo^{6+}$ ions in the zeolite were reduced and carbided to $Mo_2C$ and/or $Mo_2C$–$MoO_2$ with an oxygen deficiency and the methane activation occurred on $Mo_2C$ sites and/or $Mo_2C$–$MoO_2$ with an oxygen deficiency (6), leading to the formation of $C_2H_4$. As an alternative, we suggested that the interaction between methane and $MoO_3$ occurred during the early stage of the reaction. $MoO_3$ crystallites were reduced by methane and methane was polarized on partially reduced Mo species. The promotional effect of Ru on the catalytic performance of 2Mo/HZ catalysts can be attributed to the enhancement of partially reduced Mo species on the catalyst surface.

On the basis of above discussion, we may revise our earlier proposed mechanism (2) as follows:

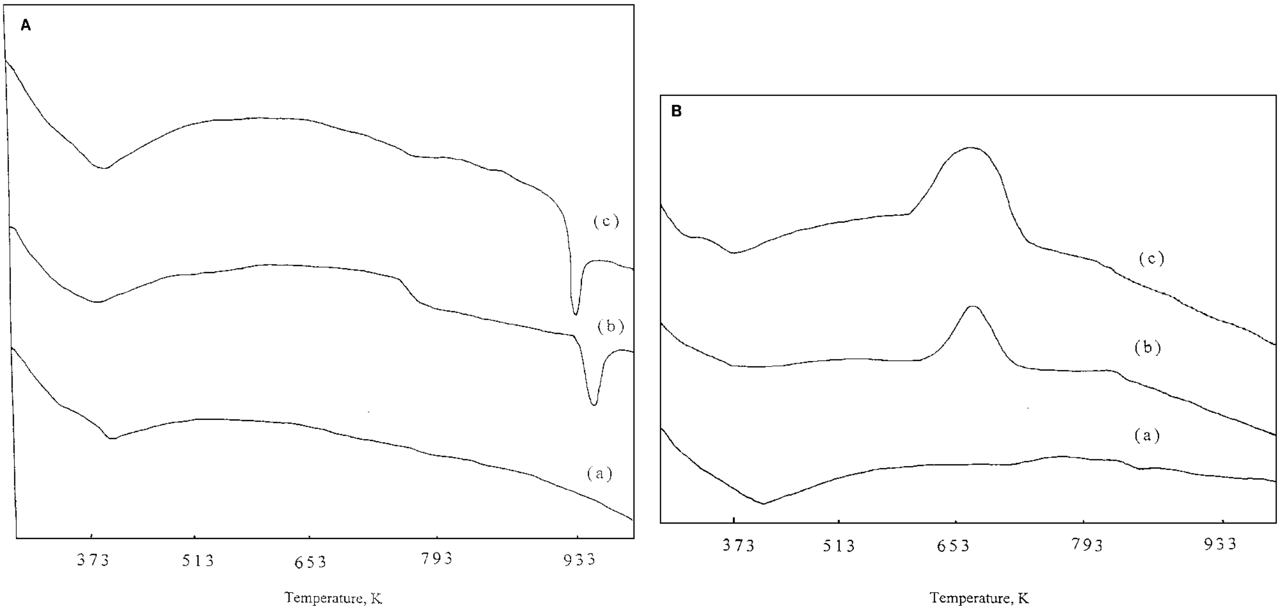
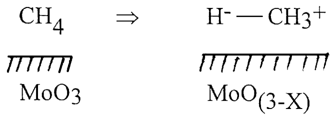
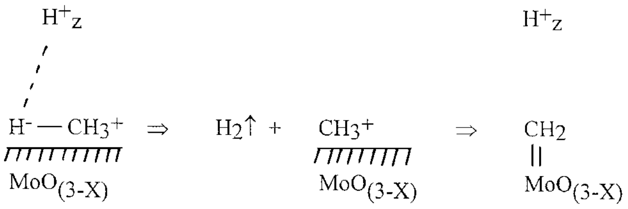


**FIG. 8.** (A) DTA profiles of HZSM-5 (a), 2Mo/HZ (b), and 2Mo–0.5Ru/HZ (c) catalysts under a methane stream. (B) DTA profiles of HZSM-5 (a), 2Mo/HZ (b), and 2Mo–0.5Ru/HZ (c) catalysts under an air stream.

(i) One of C–H bond is polarized via its interaction with the $MoO_{(3-X)}$ species in the channel.



(ii) The polarized $CH_4$ reacts with a Brønsted acid site ($H_z^+$), thereby forming a catalytic cycle of proton, accompanying by the formation of molybdenum carbene-like intermediates,



(iii)

$\overset{CH_2}{\overset{\|}{MoO_{(3-X)}}}$ dimerizes to produce $C_2H_4$.

(iv) $C_2H_4$ aromatizes on acid sites and on the sites containing Mo to produce $C_6H_6$ and $C_7H_8$.

Finally the results reported by Choudhary *et al.* (16) appears to support this mechanism.

## 4. CONCLUSION

We have previously reported, and it had been repeated by others, that methane can be activated in the absence of oxygen over 2Mo/HZ catalyst with a conversion of about 6–8% and a selectivity to aromatics of about 90% at 973 K. The acid sites and channel structure of HZSM-5 and the state and location of Mo species are crucial factors for good catalytic performance. Here, we have shown that 2Mo–Ru/HZ catalysts give a better reaction rate of methane conversion of 14.54 $nmol^{-1}\ m^{-2}$ and a better formation rate of aromatics of 2.22 $nmol^{-1}\ m^{-2}$ at 973 K and with a better stability. On the basis of the results of catalyst characterization and catalytic studies, we have shown that the possible functions of Ru in Mo–Ru/HZ catalysts are as follows:

(i) Modification of the acid sites of HZSM-5 zeolite. The amount of strong acid sites decreases with increasing Ru content in 2Mo–Ru/HZ catalysts, whereas the amount of intermediate and weak acid sites increases if Ru loading is less than or equal to 0.7%.

(ii) Promotional effect on the reduction of Mo species. The promotional effect of Ru on the reduction of Mo species is obvious and is demonstrated in TPR and DTA experiments. It appears that a proper reduction of Mo species is favorable for methane aromatization.

(iii) The enhancement of the ability of the catalyst for the splitting of the C–H bond of methane is illustrated by our DTA experiments under both $CH_4$ stream and air streams. The results further suggest that carbonaceous deposit formed during the reaction may play a positive role in the reaction.

(iv) Furthermore, the promotional effect of Ru on Mo/HZ is sensitive to the Mo/Ru atomic ratio. For a catalyst with a Mo/Ru ratio of less than 3 or higher than 7 (Mo loading is 2%), no obvious promotional effect was detected. This result supports our previous suggestion that small $MoO_3$ crystallites are active precursors for the dehydrogenation and aromatization of methane in the absence of oxygen. If the ratio of Mo/Ru is higher than 7, the amount of Ru additive is too small to affect these $MoO_3$ crystallites, whereas if the ratio of Mo/Ru is less than 3, the amount of Ru additive is too much and may change the nature of these small $MoO_3$ crystallites. Therefore, it is essential that an effective promoter should maintain the nature of these small $MoO_3$ crystallites and to cause a proper reduction of these small $MoO_3$ crystallites.

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