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# Conversion of methane to styrene over the mixed catalyst $La_2O_3 + MoO_3/HZSM$-5

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The catalytic transformation of $CH_4$ in the presence of $O_2$ over $La_2O_3$, $MoO_3/HZSM$-5 and the mixed catalyst, $La_2O_3 + MoO_3/HZSM$-5, has been investigated and compared. $MoO_3/HZSM$-5, which is known as an active catalyst for the dehydrogenation and aromatization of methane in the absence of oxygen, shows very low selectivity towards the formation of aromatic compounds in the presence of oxygen. However, the combination of $MoO_3/HZSM$-5 with $La_2O_3$ which is a very active catalyst for the production of ethane, ethylene, $CH_3$ and $CH_2$ species under the reaction conditions, provides a catalyst, $La_2O_3 + MoO_3/HZSM$-5, that is rather active for transformation of methane to styrene. At 1023 K, a methane conversion of 18.3% and styrene selectivity of 10.8% are obtained from a $CH_4/O_2$ (6/1 mole ratio) reactant gas in a feed flow rate of 3500 ml/h. Normal deuterium isotope effects on both the methane conversion reaction and the styrene formation over the $La_2O_3 + MoO_3/HZSM$-5 catalyst have been observed in the reaction.

**Keywords:** methane conversion to styrene, $La_2O_3 + MoO_3/HZSM$-5 catalyst, $CH_4/CD_4$ isotope effects

## 1. Introduction

Methane conversion to liquid fuel or fuel precursors is of great industrial interest. The catalytic conversion of methane can be carried out in several ways. Three routes that have been extensively studied include: (i) conversion of methane into syngas and its derivatives; (ii) the oxidative coupling of methane to form ethane and ethylene; (iii) direct conversion of methane in the presence of oxygen to oxygenates [1,2]. Recently, many attempts have been made to activate and to convert methane into aromatic compounds. Han and co-workers have reported the reaction of $CH_4$ with $O_2$ on HZSM-5 and metal-containing ZSM-5 catalysts in the presence of propane additives [3,4], with 1.2 $\mu$mol/(ml catalyst h) space-time yields of aromatic hydrocarbons. Propane plays an important role in the reaction. Without propane, methanol is the sole non-$CO_x$ product. The inclusion of propane additives in the feed significantly shifts product selectivity toward higher hydrocarbons. York et al. conducted the reaction of $CH_4$ with $O_2$ in a silica tube reactor without any catalyst [5]. They found that the reaction at 1220 K and 1 bar resulted in a methane conversion of about 12%, complete oxygen conversion, and a low aromatics selectivity of 2.7%, and this low production of aromatics has also been noted by ARCO [6].

Studies on $MoO_3/HZSM$-5 produce even more attractive results, showing that methane can be directly converted to benzene in the absence of $O_2$ via dehydrogenation and aromatization [7–11]. Wang et al. have reported a 100% selectivity to benzene formation at 7.2% conversion of methane over $MoO_3/HZSM$-5 at 973 K [7]. A bifunctional catalytic activation model is assumed in which methane is activated via the polarization of the $CH_4$ molecules a the $MoO_3$ sites, and the reaction of the polarized $H^-$–$CH_3^+$ occurs at the Brønsted acid sites of the HZSM-5 zeolite. Solymosi et al. have studied the catalytic behavior of supported and unsupported molybdenum compounds. They suggested that $Mo_2C$ was the active surface species which converted methane to ethylene, while the final formation of benzene occurred on the zeolite surface [8,10]. By comparing the catalytic activities of Mo/HZSM-5 before and after $NH_4OH$ extraction, Xu et al. showed that Mo species in small $MoO_3$ crystallites with the octahedral coordination was active for methane activation, while Mo species in the tetrahedrally coordinated form was less active for the reaction [11].

In the present work, a $La_2O_3 + MoO_3/HZSM$-5 mixed catalyst was applied to convert methane to styrene and other higher hydrocarbons in the presence of $O_2$ at the temperature of 1030 K. In order to study the reaction mechanism concerning the C–H bond breaking of $CH_4$ and the transformation of the reaction intermediates, the $CH_4/CD_4$ isotope effect in the methane conversion reaction is investigated over the mixed catalyst and a bifunctional catalytic activation model was proposed for the $CH_4$ conversion to styrene on $La_2O_3 + MoO_3/HZSM$-5.

## 2. Experimental

$MoO_3/HZSM$-5 with 3% Mo weight loading was prepared by impregnating HZSM-5 zeolite ($SiO_2/Al_2O_3 = 50$, mole ratio) with aqueous solution of ammo-

Table 1
The conversion of methane and the distribution of products over different catalysts [a]

| Catalyst | Conversion (%) | | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CH_4$ | $O_2$ | $C_2H_6$ | $C_2H_4$ | CO | $CO_2$ | styrene | benzene + toluene |
| $La_2O_3$ (0.2 ml) | 21.8 | 100 | 23.1 | 30.2 | 45.5 | 1.2 | 0 | 0 |
| $MoO_3$/HZSM-5 (0.2 ml) | 14.9 | 100 | 10.4 | 18.9 | 68.1 | 0 | 1.6 | 1.0 |
| $La_2O_3$ (0.2 ml) + $MoO_3$/HZSM-5 (0.2 ml) | 18.3 | 100 | 20.0 | 15.3 | 50.8 | 0 | 10.8 | 3.1 |

[a] Reaction temperature, 1023 K. Composition of reactant gas, $CH_4/O_2 = 6/1$ (mole ratio). Feed flow rate of reactant gas 3500 ml/h.

nium heptamolybdate. The sample was then dried in air at 383 K for 10 h and calcined at 873 K for 6 h in air. $La_2O_3$(99.9%) used in the experiment was a product of Aldrich. Both $MoO_3$/HZSM-5 and $La_2O_3$ were pressed, crushed and sieved to form 40–60 mesh pellets. Catalytic tests were performed in a fixed bed continuous-flow quartz tube reactor (4.8 mm i.d.) at 1 atm of reactant gas pressure. The amount of the catalyst applied for the $La_2O_3$ and $MoO_3$/HZSM-5 testing is 0.2 ml, respectively. The $La_2O_3$ + $MoO_3$/HZSM-5 catalyst was composed by well mixing 0.2 ml each of $MoO_3$/HZSM-5 and $La_2O_3$ pellets. A $CH_4/O_2$ mixture gas with a 6 : 1 mole ratio was passed through the catalyst bed at a flow rate of 3500 ml/h and the catalytic reaction temperature was 1023 K. Effluents were analyzed using a Balzers quadrupole mass spectrometer (Prisma QMS 200). The calibration of the quantitative analysis was done by gas chromatography. The conversion of methane and the selectivity to reaction products were calculated on the basis of carbon number balance. The data were taken after the reaction run for at least 2 h to reach stable performance of the catalysts. In the studies of the kinetic isotope effect on the reaction rate, a feed consisting of $CH_4$ ($CD_4$)/$O_2$/He (6/1/7, mole ratio) was applied. After the reaction of $CH_4/O_2$/He over the catalyst has reached the steady state, the $CH_4$ in the feed was replaced by $CD_4$. The conversion of $CD_4$ and the selectivities to the relative products were calculated from the data taken after the reaction reached the stable state.

## 3. Results and discussion

### 3.1. *Methane oxidation reaction on $La_2O_3$, $MoO_3$/HZSM-5, and mixed $La_2O_3$–$MoO_3$/HZSM-5 catalysts*

Table 1 summarizes the results for the oxidation of methane over $La_2O_3$, $MoO_3$/HZSM-5 and mixed catalyst consisting of $La_2O_3$ and $MoO_3$/HZSM-5. For $La_2O_3$, under the cofeed reaction conditions of $CH_4/O_2 = 6/1$ (mole ratio), 21.8% of $CH_4$ is found to be converted to $C_2H_6$ and $C_2H_4$, in addition to CO and $CO_2$ with no aromatic product, indicating $La_2O_3$ is an effective catalyst for oxidative coupling of methane to ethane and ethylene. For $MoO_3$/HZSM-5, which has been reported to be a rather active catalyst for the dehydrogenation and aromatization of methane in the absence of oxygen [7–11], carbon monoxide is the main product when methane is cofed with oxygen, and the product selectivity toward aromatic compound is very low. When $CH_4$ and $O_2$ are cofed through the catalyst bed consisting of well mixed $La_2O_3$ and $MoO_3$/HZSM-5, the distribution of the products changes greatly as compared with that of the reaction catalyzed by $La_2O_3$ or $MoO_3$/HZSM-5. At the methane conversion of 18.3%, a styrene selectivity of 10.8% together with 3.1% of other aromatic compounds is obtained. The space-time yield of styrene is estimated to be 0.17 mmol/(ml catalyst h). Since no aromatic compound was detected for the reaction over the $La_2O_3$ catalyst, it can be inferred that aromatic compounds detected over the $La_2O_3$ + $MoO_3$/HZSM-5 catalyst under similar reaction conditions must originate from reactions on the $La_2O_3$ + $MoO_3$/HZSM-5 catalyst but not from the gas phase reaction. The production of styrene from the gas phase reaction of $CH_4$ was reported to occur only at temperatures higher than 1170 K [5] whereas the present experiments were performed at 1023 K. As shown in figure 1 the proper temperature range for the styrene formation is 1023–1073 K on the $La_2O_3$ + $MoO_3$/HZSM-5 catalyst.

It is interesting to note that the oxidation reaction of methane over the above three types of catalysts all result in a very small amount of $CO_2$ in the reaction product. This is most probably due to the low space velocity of reactant gas ($1.75 \times 10^4$ $h^{-1}$ for both $La_2O_3$ and $MoO_3$/HZSM-5, and $8.75 \times 10^3$ $h^{-1}$ for $La_2O_3$ + $MoO_3$/HZSM-5 catalyst), resulting in the $CO_2$ produced having enough time to take part in successive reaction with hydrocarbons ($CH_4$, $C_2H_6$ and $C_2H_4$) in the gas stream to produce CO. Note also that in table 1 the same amount (0.2 ml) of $La_2O_3$ and $MoO_3$/HZSM was used in all three experiments. This was to show that the great change in product distribution was caused by simply mixing two types of catalysts together, despite that the space-velocity was not kept constant due to the different total amount of the catalyst used. In another experiment using a catalyst composed of both $La_2O_3$ + $MoO_3$/HZSM-5 but prepared by a different method (impregnation rather than mechanical mixing) little styrene was observed though the space-velocity was kept constant. This appears to indicate that the production of styrene is

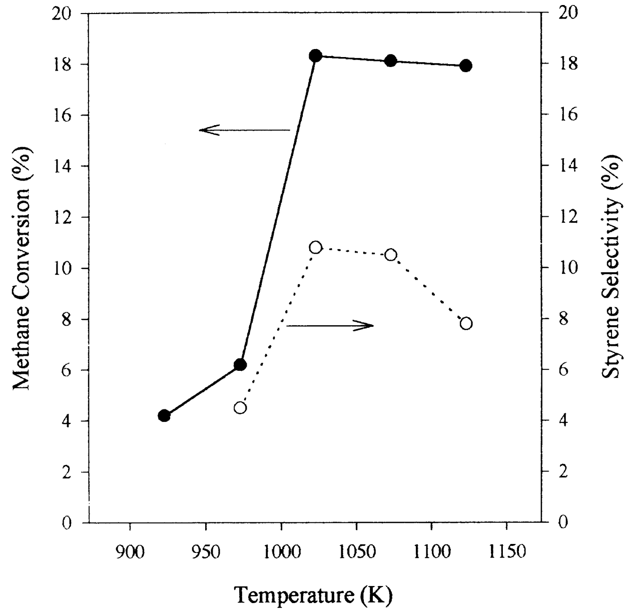

Figure 1. Methane conversion (●) and styrene selectivity (○) as a function of reaction temperature over the mixed $La_2O_3$(0.2 ml) + $MoO_3$/HZSM-5(0.2 ml) catalyst. The reaction was conducted under conditions: $P = 1$ atm; composition of reactant gas, $CH_4/O_2 = 6/1$ (mole ratio); feed flow rate of reactant gas, 3500 ml/h.

not due to smaller space-velocity but due to the synergism between $La_2O_3$ and $MoO_3$/HZSM, and most probably through $C_2H_4$ (or its radical) gas-phase propagation (see infra).

Oxygen plays an important role in the conversion of methane to styrene over the mixed catalysts, $La_2O_3 + MoO_3$/HZSM-5. When $O_2$ in the inlet flow was abruptly replaced by He, styrene disappeared in a very short time period from the effluent stream (see figure 2). After the inlet flow was switched back to the initial reactant mixtures $CH_4/O_2$, the initial steady-state catalytic activity was recovered. It is worthy to note that ethane responses faster than styrene in the process.

As has been shown in table 1, $La_2O_3$ is an effective catalyst for methane oxidative coupling reaction to form ethane and ethylene in the presence of oxygen. It is generally accepted [12,13] that in the methane oxidative coupling, methane reacts with the active oxygen species on the catalyst surface to form a methyl radical (·$CH_3$), which emanates mostly into the gas phase and couples to form ethane. Ethylene is produced from dehydrogenation of ethane and coupling of carbene species formed by further dehydrogenation of the methyl radical. It is interesting to note that ethane, ethylene, methyl radical and carbene species, the products or the intermediates of the $CH_4 + O_2$ reaction catalyzed by $La_2O_3$, are the active species that can be easily transformed to aromatic hydrocarbons over the catalysts consisting of metal oxide and HZSM-5 [14]. Over the $MoO_x$/HZSM-5, ethylene is identified as a primary product that can be subsequently converted to aromatic compounds on the

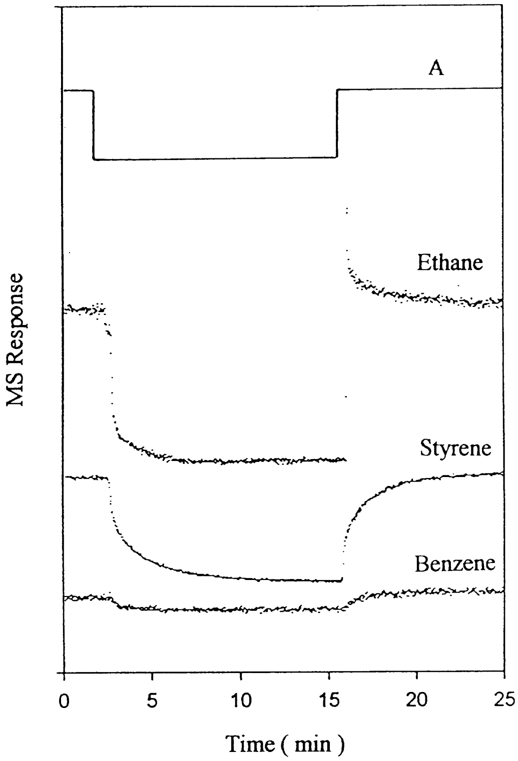

Figure 2. Plots of the reaction products (ethane, styrene and benzene) as measured by mass spectrometry (MS) versus time. At the initial stage of the reaction $CH_4$ and $O_2$ (6/1 mole ratio) mixture gas was passed through the catalyst $La_2O_3$(0.2 ml) + $MoO_3$/HZSM-5(0.2 ml) at 1023 K, 1 atm and 3500 ml/h. By pulse injection, $O_2$ in the inlet flow was replaced by He for a short period and then switched back to $O_2$, as shown in curve "A". The MS response of the ethane, styrene and benzene in the effluent was then plotted separately as function of the He injection.

dehydrogenation and aromatization reaction of methane [9,10]. The studies of Ono et al. have shown that ethane can be converted to aromatic hydrocarbons [15]. Over $ZnO_x$/HZSM-5 catalyst, an ethane conversion of 52% and a yield of aromatics at 31% have been obtained. The methyl radical and carbene species are the most common intermediates that have been suggested in mechanism studies of the methane aromatization reaction. As pointed out by Solymosi et al., a good active center in the conversion of methane to benzene over $MoO_3$/HZSM-5 should play a role in activating the methane molecule to produce $CH_3$ and $CH_2$ fragments [10]. Though under the $CH_4$ and $O_2$ cofeed reaction conditions $La_2O_3$ is absolutely not a good catalyst for the transformation of methane to acromatic compounds, its combination with $MoO_3$/HZSM-5, a rather active catalyst for the dehydrogenation and aromatization of methane in the absence of oxygen [7–11], results in a rather effective catalyst for direct transformation of methane to styrene and other higher hydrocarbons. A bifunctional activation model may be therefore assumed that methane is activated by $La_2O_3$, and some of ethane, ethylene, methyl radical and carbene species produced

Table 2
Kinetic isotope effect for the oxidation of methane to styrene over catalyst consisting of mixed $La_2O_3$ and $MoO_3/HZSM\text{-}5$ [a]

| Temperature (K) | $R_{\text{all}}^{CH_4}/R_{\text{all}}^{CD_4}$ | $R_{C_2H_6}^{CH_4}/R_{C_2D_6}^{CD_4}$ | $R_{C_2H_4}^{CH_4}/R_{C_2D_4}^{CD_4}$ | $R_{\text{styrene}}^{CH_4}/R_{\text{styrene}}^{CD_4}$ |
|---|---|---|---|---|
| 1023 | 1.5 | 1.6 | 2.6 | 2.6 |
| 1063 | 1.3 | 1.3 | 2.0 | 2.1 |

[a] Composition of influent, $CH_4(CD_4)/O_2/He = 6/1/7$ (mole ratio). GHSV = $1.75 \times 10^5$ $h^{-1}$, $R_{\text{all}}^{CH_4(CD_4)}$ is the overall rate of $CH_4(CD_4)$conversion. $R_X^{CH_4(CD_4)}$ denotes the rate of $CH_4(CD_4)$ conversion to X.

on the $La_2O_3$ may migrate or diffuse to the surface of $MoO_3/HZSM\text{-}5$ where they can be further transformed to aromatic compounds.

### 3.2. *$CH_4/CD_4$ isotope effect in the methane oxidation on mixed $La_2O_3$ and $MoO_3/HZSM\text{-}5$ catalyst*

To elucidate the reaction mechanism, $CH_4/CD_4$ isotope effects in the oxidation of methane to styrene over mixed $La_2O_3$ and $MoO_3/HZSM\text{-}5$ catalyst were studied. In this experiment, $CH_4/O_2/He$ (6/1/7 mole ratio) was cofed over the mixed catalysts. After the reaction had reached a steady state, $CH_4$ in the feed gas was then replaced by $CD_4$. The results calculated based on the measured products distribution are presented in table 2. It can be seen that the overall rate of methane conversion is reduced upon replacing $CH_4$ by $CD_4$, with apparent kinetic isotope effect ($R_{\text{all}}^{CH_4}/R_{\text{all}}^{CD_4}$) being 1.5 at the reaction temperature of 1023 K. This result agrees well with previous data [16–19] obtained for oxidative dimerization of methane and may imply that the rate-determining step involved in the oxidation conversion reaction of methane is the breaking of the C–H bond of the $CH_4$ molecule over the catalyst. It is noted in table 2 that the kinetic isotope effects are temperature dependent, decreasing with increasing temperature as expected [19]. The apparent kinetic isotope effects for ethylene production ($R_{C_2H_4}^{CH_4}/R_{C_2D_4}^{CD_4}$) are found to be greater than those of the overal rate of methane conversion ($R_{\text{all}}^{CH_4}/R_{\text{all}}^{CD_4}$), and those of ethane production ($R_{C_2H_6}^{CH_4}/R_{C_2D_6}^{CD_4}$). This is similar to the results reported in the methane oxidative coupling reaction [16–18]. This may appear to be caused by two successive effects, one in the conversion of methane to ethane, the second in the conversion of ethane to ethylene. Within the error limits the kinetic isotope effect of styrene production ($R_{\text{styrene}}^{CH_4}/R_{\text{styrene}}^{CD_4}$) is the same as that for ethylene production ($R_{C_2H_4}^{CH_4}/R_{C_2D_4}^{CD_4}$). It gives us a clue that the formation of styrene in this catalytic system may go through the similar C–H breaking route as the formation of ethylene:

$$CH_4 \rightarrow \cdot CH_3 \rightarrow CH_3CH_3 \rightarrow CH_2CH_2 \rightarrow \text{styrene} \quad (1)$$

$$CH_4 \rightarrow \cdot CH_3 \rightarrow (CH_2)_{\text{ad}} \rightarrow CH_2CH_2 \rightarrow \text{styrene} \quad (2)$$

$$CH_4 \rightarrow \cdot CH_3 \rightarrow (CH_2)_{\text{ad}} \rightarrow \text{styrene} \quad (3)$$

## 4. Conclusions

A catalyst consisting of $La_2O_3 + MoO_3/HZSM\text{-}5$ was applied to convert methane to styrene in the presence of $O_2$. 0.17 mmol/(ml catalyst h) space-time yield of styrene was obtained at 1023–1073 K. It is assumed that some of ethane, ethylene, methyl radical and carbene species produced on the $La_2O_3$ may migrate or diffuse to the surface of $MoO_3/HZSM\text{-}5$ on which they can be further transformed to aromatic compounds. Normal deuterium isotope effects have been observed over the $La_2O_3 + MoO_3/HZSM\text{-}5$ catalyst both for the methane conversion reaction and for the styrene formation, which may indicate that the C–H bond breaking of the $CH_4$ molecules is the reaction rate-determining step.

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