Conversion of methane to styrene over the mixed catalyst 
La$_2$O$_3$ + MoO$_3$/HZSM-5

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The catalytic transformation of CH$_4$ in the presence of O$_2$ over La$_2$O$_3$, MoO$_3$/HZSM-5 and the mixed catalyst, La$_2$O$_3$ + 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$_2$O$_3$ 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$_2$O$_3$ + 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$_2$O$_3$ + MoO$_3$/HZSM-5 catalyst have been observed in the reaction.

**Keywords:** methane conversion to styrene, La$_2$O$_3$ + 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 at the MoO$_3$ sites, and the reaction of the polarized H–CH$_3$ occurs at the Bronsted 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$_2$C 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$_4$OH 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$_2$O$_3$ + 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$_2$O$_3$ + 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$_2$O$_3$ = 50, mole ratio) with aqueous solution of ammo-
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. La2O3 (99.9%) used in the experiment was a product of Aldrich. Both MoO3/HZSM-5 and La2O3 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 La2O3 and MoO3/HZSM-5 testing was 0.2 ml, respectively. The La2O3 + MoO3/HZSM-5 catalyst was composed by well mixing 0.2 ml each of MoO3/HZSM-5 and La2O3 pellets. A CH4/O2 mixture gas with a 6 : 1 molar 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 CH4 (CD4)/O2/He (6/1/7, mole ratio) was applied. After the reaction of CH4/O2/He over the catalyst has reached the steady state, the CH4 in the feed was replaced by CD4. The conversion of CD4 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 La2O3, MoO3/ HZSM-5, and mixed La2O3-MoO3/HZSM-5 catalysts

Table 1 summarizes the results for the oxidation of methane over La2O3, MoO3/ HZSM-5 and mixed catalyst consisting of La2O3 and MoO3/HZSM-5. For La2O3, under the co-fed reaction conditions of CH4/O2 = 6/1 (mole ratio), 21.8% of CH4 is found to be converted to C2H6 and C2H4, in addition to CO and CO2 with no aromatic product, indicating La2O3 is an effective catalyst for oxidative coupling of methane to ethane and ethylene. For MoO3/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 CH4 and O2 are cofed through the catalyst bed consisting of well mixed La2O3 and MoO3/HZSM-5, the distribution of the products changes greatly as compared with that of the reaction catalyzed by La2O3 or MoO3/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 La2O3 catalyst, it can be inferred that aromatic compounds detected over the La2O3 + MoO3/HZSM-5 catalyst under similar reaction conditions must originate from reactions on the La2O3 + MoO3/HZSM-5 catalyst but not from the gas phase reaction. The production of styrene from the gas phase reaction of CH4 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 La2O3 + MoO3/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 CO2 in the reaction product. This is most probably due to the low space velocity of reactant gas (1.75 × 10^4 h⁻¹ for both La2O3 and MoO3/HZSM-5, and 8.75 × 10^3 h⁻¹ for La2O3 + MoO3/HZSM-5 catalyst), resulting in the CO2 produced having enough time to take part in successive reaction with hydrocarbons (CH4, C2H6 and C2H4) in the gas stream to produce CO. Note also that in table 1 the same amount (0.2 ml) of La2O3 and MoO3/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 La2O3 + MoO3/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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<tbody>
<tr>
<td>CH4 O2</td>
<td></td>
<td>C2H6 C2H4 CO CO2 styrene benzene + toluene</td>
</tr>
<tr>
<td>La2O3 (0.2 ml)</td>
<td>21.8</td>
<td>23.1 30.2 45.5 1.2 0 0</td>
</tr>
<tr>
<td>MoO3/HZSM-5 (0.2 ml)</td>
<td>14.9</td>
<td>10.4 18.9 68.1 0 1.6 1.0</td>
</tr>
<tr>
<td>La2O3 (0.2 ml) + MoO3/HZSM-5 (0.2 ml)</td>
<td>18.3 100</td>
<td>20.0 15.3 50.8 0 10.8 3.1</td>
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