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# A new phenomenon in the induction period of the methane dehydroaromatization reaction

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**The induction period of dehydroaromatization of methane to benzene over Mo/HZSM-5 had been investigated in real-time by the resonant-enhanced two-photon ionization (RE2PI) technique; it is remarkable that there is a small amount of benzene formed in the early stage of the induction period; we suggest that the trace amount of benzene was caused by the reduction of the original $Mo^{6+}$ ion during the induction period and the $Mo^{6+}$ species has a slight catalytic activity for methane–benzene conversion.**

Direct conversion of methane to higher hydrocarbons, particularly to aromatics such as benzene, toluene, and naphthalene under non-oxidative conditions has received considerable recent attention.[1–3] The dehydroaromatization reaction of methane to benzene over the Mo/HZSM-5 catalysts in flow reactors has been carried out and achieved some attractive results, such as a methane conversion of 7–8% with 70–80% selectivity to benzene. Although a similar catalytic performance has been reported by several groups[2,4–7] for methane conversion over Mo/HZSM-5, differing active sites, reaction mechanisms and reaction intermediates have been proposed by various investigators. Xu *et al.*[6] suggest that $MoO_3$ may be involved as the catalytically active center, and that dimerization of a $CH_2{=}MoO_3$ species occurs to produce ethylene as the reaction intermediate. Later they further proposed that the active center was partially reduced molybdenum oxide species $MoO_{(3-x)}$. Lin *et al.*[7] supposed that the activation of methane to form $CH_3\cdot$ radicals occurred *via* a synergistic action between $MoO_x$ and the Brønsted acid site, and the $CH_3\cdot$ radicals dimerized to form ethane as the primary product. Wang *et al.*[8] reported that the reaction is characterized by an induction period, prior to the initiation of benzene formation, during which $Mo_2C$ is formed and coke deposition occurs, as revealed by X-ray photoelectron spectroscopy (XPS) measurements. Solymosi *et al.*[9] suggested that $Mo_2C$–$MoO_2$ with an oxygen deficiency was responsible for the production of ethylene from methane, and ethylene was then converted to benzene on the acidic sites of HZSM-5 support. This reaction is characterized by an induction period, prior to the initiation of benzene production, during which the catalyst surface undergoes physical and chemical changes and gradually forms catalytic active sites, so it is without doubt that the amount of the reaction products varies with time and different detective methods will give rise to different reaction mechanisms.

The resonant-enhanced multi-photon ionization (REMPI) spectrum technique has a high sensitivity and good selectivity. It has been widely used to study spectrum structures and energy-transfer dynamics of atoms, molecules and free radicals.[10,11] In REMPI, we exploit a tunable laser to selectively ionize the product molecules and collect the signals of the resulting photoelectrons *via* electrodes. Based on the ion signals of specified reactant or products, we can instantly monitor the changes of the content of the objective species in the reaction product mixture, monitoring the course of catalytic reaction. In this paper, we investigated in real-time the induction period of the reaction by RE2PI (resonant-enhanced 2-photon ionization) technique and new phenomena have been observed.

According to the resonant-enhanced two-photon ionization spectrum of benzene, we use UV light at 259.5 nm obtained from the frequency-doubled output by the BBO crystal of a dye-laser (Lambda-Physick model FL2002) operating with Coumarin 503 dye, which is pumped by XeCl (Xe/HCl/He) excimer. A Photodiode was used to monitor the wave of laser energy. Through the amplifier and BOXCAR, ion signals produced by the two electrodes were collected by micro-computer. Typical dye laser pulse energy was attenuated to ~ 50 μJ, before accessing detection windows. All ionization signal measurements were an average of 6 laser pulses, in order to remove pulse to pulse signal variations caused by fluctuations of pump laser energies.

The catalyst was prepared by impregnating an aqueous solution containing the desired amount of ammonium heptamolybdate $[(NH_4)_6Mo_7O_{24}]$ in a vacuum environment at rt for 24 h, followed by drying for 4 h at 120 °C and then calcining for 4 h at 500 °C in air. The calcined samples were crushed and sieved to 60/80 mesh granules. Since all of the Mo-containing solution was deposited onto HZSM-5 support during drying, the Mo content in the final catalyst was assumed to be the same as the total Mo content of the solution.

Reactions were carried out in a fixed bed continuous up-flow quartz reactor with an inter diameter of 7 mm and using 0.1 g of catalyst. The upper section of the reactor is a pair of detection electrodes and detecting windows and the middle is a catalyst bed. Temperature was measured by a type K thermocouple located inside a quartz sheath in contact with the catalyst bed. The reactor effluent was sampled using transfer lines held at 400 K, avoiding gas-product condensations. The hourly space velocity of methane was 1500 ml $g^{-1}$ $h^{-1}$. Reactant and flush gases which included 50% $CH_4$–Ar, Ar (99.99%), respectively, were used with further purification and gas flows were regulated by mass flow controllers. The catalyst was first heated under the flow reactor in a stream of Ar from rt to 973 K for 1 h, maintained at a temperature of 973 K for 0.5 h, and then the 50% $CH_4$–Ar reactant gas mixture was introduced into the reactor. The reaction mixtures were also analyzed by online Gas Chromatography (Shanghai Xianchuang Instrument Factory, Model GC-8810) using a column SE-30 and hydrogen flame ionization detector. All studies were carried out at atmospheric pressure and at 973 K.

The aromatization reaction of methane over 6 wt% Mo/HZSM-5 was studied at 973 K by RE2PI techniques and experimental results are shown in Fig. 1. It is obvious to see from Fig. 1(A) that the dehydroaromation reaction of methane to benzene over Mo/HZSM-5 zeolite does have an induction period for $CH_4$ activation. The results of RE2PI are almost the same as the results of GC, which proves that REMPI is a reliable technique to study this reaction. But it is noteworthy that there

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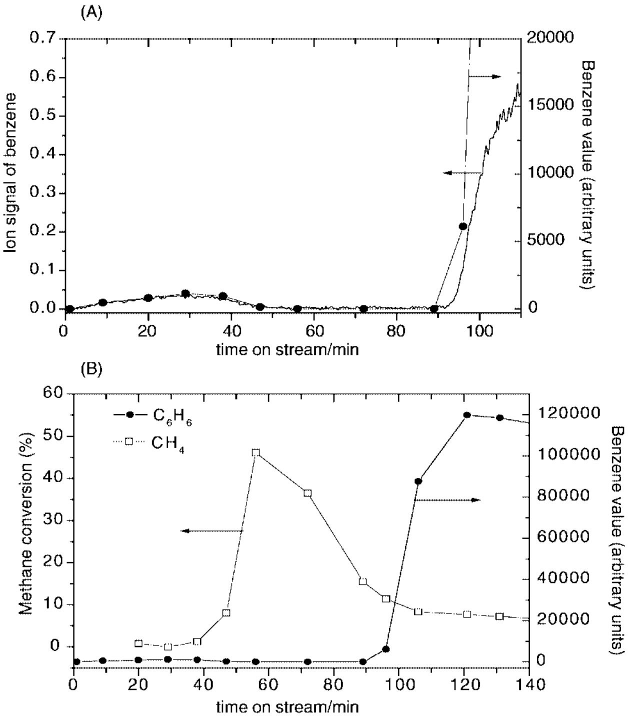

**Fig. 1** (A) Benzene RE2PI and GC results *versus* reaction time over 6 wt% Mo/HZSM-5 at 973 K, 1 atm and GHSV = 1500 $h^{-1}$. — denotes ion signal results by RE2PI, — ● — denotes GC results. (B) Methane conversion and benzene relative peak area by GC method over 6 wt% Mo/HZSM-5 at 973 K, 1 atm, and GHSV = 1500 $h^{-1}$.

is a small amount of benzene formed at the very beginning of the reaction. Though compared with the amount of benzene after the induction period, the amount of benzene in the early stage of the induction period is negligible; it is an important hint for the reaction mechanism. This phenomenon has never been reported in previous studies. According to Fig. 1(A), we divided the induction period into two continuous sections; one is from 0 to 50 min and the other is from 50 to 90 min. In section one, when reactant gases were contacted with the catalyst, benzene was immediately formed. With the increase of reaction time, the benzene signal grows slowly. After reaching its highest point at about 27 min, the benzene signal began to decrease steadily. At the end of section one, there is no benzene signal. In section two, there is no signal of benzene. From Fig. 1(B), we see that the conversion of methane in these sections is totally different. In section one, the conversion of methane is 1–2%; in section two, the conversion of methane increases with time and reaches its highest point, 31%, at about 52 min, and then decreases. After section two, a significant amount of benzene was produced, while the conversion of methane almost keeps constant at ~ 7%. The signal of benzene from GC in Fig. 1(B) is the same with in Fig. 1(A), except the unit. Under the same reaction conditions, we repeated the experiment with 3.5 wt% Mo/HZSM-5 and 12 wt% Mo/HZSM catalysts and achieved similar results. The only differences are the lengths of induction period for the three catalysts.

As to the mechanism of methane aromatization reaction to benzene over Mo/HZSM-5 catalyst without oxidant, we suggest that the limited generation of benzene in the induction period section two was produced during the reduction of the original $Mo^{6+}$ species. Less than 2% of the incoming methane was converted and only a trace amount of benzene was formed, showing that the $Mo^{6+}$ species has a slight catalytic activity for methane–benzene conversion. The $Mo^{6+}$ ion was reduced to lower oxidation state Mo species in this section. However in section two, a large amount of methane interacted with the catalyst without generation of benzene, suggesting that large amounts of carbon deposited on the catalyst in the course of high temperature methane conversion. The catalytic active sites were converted from $Mo^{6+}$ species, which are unstable and easily reduced, to lower oxidation states of Mo species, which are very stable in a non-oxidizing atmosphere.

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