

High-throughput screening of HZSM-5 supported metal-oxides catalysts for the coupling of methane with CO to benzene and naphthalene

Hua Wang, Zhongmin Liu *, Jianghan Shen, Hongchao Liu, Jinling Zhang

*Natural Gas Utilization and Applied Catalysis Laboratory, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, PR China*

Received 10 August 2004; accepted 16 February 2005
Available online 16 March 2005

Abstract

High-throughput screening of HZSM-5 supported metal-oxides catalysts were carried out for the coupling reaction of methane with CO to aromatics in a multi-stream reactor system. Zn/HZSM-5 and Mo/HZSM-5 were observed to be rather effective for the catalytic formation of aromatics from the coupling reaction of methane with CO. Temperature-programmed reaction has further proven the efficiency of the coupling of methane and CO over Zn/HZSM-5 catalyst. The results were also validated in a conventional fixed-bed reactor coupled with GC. The results propose that the coupling methane with CO toward benzene and naphthalene can be catalyzed by Zn/HZSM-5 at 500 °C. Both methane and CO are needed for the formation of reactive coke on the catalyst, and the reactive coke may be the initial product in the producing of hydrocarbons.

© 2005 Elsevier B.V. All rights reserved.

Keywords: CO; Coupling; High-throughput screening; Methane; Zn/HZSM-5

1. Introduction

Much attention has been paid to the conversion of methane into useful chemicals and easily transportable liquid fuels, based on the consideration that the abundant methane resources will play more significant roles in the production of energy and chemicals in new century. Direct conversion of methane to fuels or chemicals is particularly expected, as compared with indirect routes; however, the reaction merely occurs at high temperatures, possibly due to the thermodynamic limitations.

Choudhary et al. [1] first reported the activation of methane over H-GaAlZSM-5 in the presence of either

alkenes or higher alkanes at low temperatures, yielding higher hydrocarbons and aromatics at high-rate conversions. Subsequently, other researchers demonstrated that the conversion of methane could be remarkably improved by the coupling reaction of methane with ethylene over Ag/Y or HZSM-5 ion-exchanged with various metal cations [2], and that the transformation of methane into aromatic hydrocarbons was activated with liquefied-petroleum-gas (LPG) over Zn/ZSM-11 zeolite [3] under mild conditions.

In 1997, Naito et al. [4] observed the selective formation of benzene in the CH₄ + CO reaction catalyzed by Rh/SiO₂ under atmospheric pressure, where benzene resulted from the contribution of both CH₄ and CO together, and carbon atoms in benzene mainly came from CO [5]. Since the first report made by Wang et al. [6], the direct dehydrocondensation of methane to benzene in the absence of oxygen has been widely

* Corresponding author. Tel.: +86 411 84685510; fax: +86 411 84691570.

E-mail address: liuzm@dicp.ac.cn (Z. Liu).

studied on Mo/HZSM-5, which, however, easily suffered from a rapid deactivation because of the coke deposition [7,8]. To reduce coking on the catalysts, some efforts have been accordingly made [9–11], e.g., the addition of a few percentages of CO and CO₂ into methane-feed-gas significantly promoted the stability of the methane dehydrocondensation reaction toward aromatics on Mo/HZSM-5, as compared with the case using pure methane as the reactant [12].

In the present work, we select the commonly used metal compounds to prepare the HZSM-5 supported samples and screen the catalytic activity of these samples for the coupling reaction of methane and CO by a high-throughput technique. It was observed that over Zn/HZSM-5, benzene and naphthalene were the dominant products, together with a small amount of toluene under atmospheric pressure, and that the coupling reaction could effectively take place at the temperature as low as 500 °C, notably lower than the temperature (700 °C) required for the formation of benzene with pure methane [13].

2. Experimental

HZSM-5 supported catalysts were prepared by wet impregnation of solid HZSM-5 grains (40–60 mesh, Si/Al = 25, Fushun China) with metals-containing solutions controlled by a computer-assisted Varian sample preparation system (model SPS-5). The raw materials used included: TiCl₃, VOC₂O₄, Cr(NO₃)₃ · 9H₂O, Mn(NO₃)₂, Fe(NO₃)₃, Co(NO₃)₂ · 6H₂O, Ni(NO₃)₂ · 6H₂O, Cu(NO₃)₂ · 3H₂O, Zn(NO₃)₂ · 6H₂O, Y(NO₃)₃, Zr(NO₃)₄ · 5H₂O, (NH₄)₆Mo₇O₂₄ · 5H₂O, RuCl₃ · 3H₂O, RhCl₃, PdCl₂, AgNO₃, In(NO₃)₂, SnCl₂ · 2H₂O, SbCl₃, La(NO₃)₃ · *n*H₂O, (NH₄)₅H₅[H₂(WO₄)₆] · H₂O, H₂IrCl₆, H₂PtCl₆ · 6H₂O, Pb(NO₃)₂, AuCl₃ · HCl · 4H₂O, Ce(NO₃)₃ · 6H₂O, Nd(NO₃)₃ · *n*H₂O, Pr₆O₁₁, Sm₂O₃, Gd₂O₃, Tb₄O₇, Th(NO₃)₄ · 4H₂O, and UO₂(CH₃COO)₂ · 2H₂O. Most of primary compounds were dissolved in water to prepare aqueous solutions, with some exceptions that TiCl₃ was dissolved in ethyl alcohol, metal chloride in diluted hydrochloric acid and metal oxides in diluted nitric acid. Then, the impregnation was carried out at room temperature for 24 h with adding the required quantity of metals-containing solutions in a tube of 100 ml. Each time, 20 g of freshly dried HZSM-5 was used as the support. Thereafter, the mixture was directly dried at 120 °C for 12 h, followed by calcination at 550 °C for 4 h in air. The compositions (wt%) of catalysts were determined by X-ray fluorescence spectroscopy on a Philips Magix 601 apparatus. X-ray powdered diffraction patterns were recorded on a Rigaku D/max-rb instrument with a Ni-filtered Cu K α radiation.

In the screening experiments of catalysts, all of 40 fresh samples (about 80 mg for each one), and quartz

grains for blank test, were loaded into the respective tube reactor in a multi-stream reactor system [14]. The catalyst samples were, subsequently, pretreated at desired reaction temperatures for 2 h in the flow of helium. After that, the reaction gas with a composition of 12.5% methane, 37.5% CO, and 50% helium controlled via a mass-flow controllers was introduced into the reactor. The space velocity of methane/catalyst was kept at about 8000 h⁻¹, and the effluent of each tube reactor was detected by a multi-stream mass spectrometer screening system [15]. To accelerate the acquisition of data, only selected mass ions were detected during the testing process, in which the *m/e* mass numbers were: 2 (H₂), 16 (methane), 27 (ethylene), 28 (CO), 78 (benzene), and 128 (naphthalene), respectively. To remove the remainders in the pipeline, the system was flushed for 6 s before acquiring the data of each stream. The sampling time was 18 s, which was adequate for the acquisition of 3–4 sets of data in the present work, enabling the screening of the entire 40-sample library within 16 min.

In the validation experiment, the catalyst was tested under atmospheric pressure in a conventional fixed-bed reactor equipped with a quartz tube loading 0.6 g catalyst with 40–60 mesh. After flushing with N₂ at the reaction temperature for 30 min, a feed gas mixture of CH₄, CO with He (as internal standard for analysis) was introduced into the reactor at a flow rate of 10 ml/min [space velocity = 1000 ml (g h)⁻¹] through a mass flow controller.

Hydrocarbon products were analyzed by an on-line gas chromatography (FID detector, Porapak-Q column). He, CO, CH₄ and CO₂ were sampled simultaneously by a ten-way sampling valve heating to 250 °C and analyzed by the same GC with TCD detector and an activated carbon column. Condensable products such as benzene, toluene and naphthalene were identified by using an off-line GC–MS. The conversion of methane and CO, selectivity of products and coke formed on the catalysts were calibrated by the equations reported by Liu et al. [16].

3. Results and discussion

Fig. 1 shows the signal intensity of the mass ions detected on-stream in the coupling of methane with CO at 650 °C for 5 h, where the intensity of some ions inclusive of H₂, C₂H₄, C₆H₆, and C₁₀H₈, had been multiplied by proper coefficients. Note that due to the fluctuation of MS signals, it is not easy to discriminate the coupling reaction from the signal change of methane and/or CO. The formation of H₂ was observed over the Pd/HZSM-5 catalyst, showing the dehydrogenation of methane under experimental conditions. Over the Mo/HZSM-5 catalyst that is a traditional catalyst for the methane dehydroaromatization [9–11], ethylene,

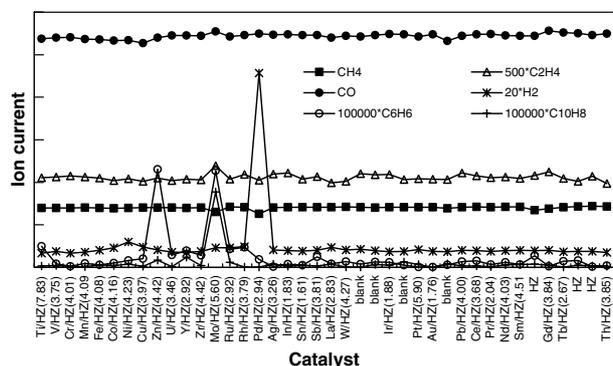


Fig. 1. Signal intensity of the mass ions detected on-stream in the coupling of methane with CO over HZSM-5 supported metal-oxides catalysts at 650 °C for 5 h.

benzene and naphthalene could be clearly detected. Interestingly, benzene and naphthalene were formed over Zn/HZSM-5, with a product distribution different from that over Mo/HZSM-5. Under identical conditions, the introduction of either methane or CO alone into the reaction system did not cause any detectable signal of benzene, suggesting that the coexistence of methane and CO was required for the yield of benzene over Zn/HZSM-5. When using SiO₂, Al₂O₃, 13X, and activated carbon as the supports instead of HZSM-5, no any signal of aromatics was detected over Zn- and Mo-containing catalysts, indicating the importance of an acidic support like HZSM-5 for the coupling of methane with CO.

Fig. 2 shows the temperature-programmed coupling reaction over Zn/HZSM-5 as a function of temperature, where likewise some signals were multiplied by proper coefficients as well. Prior to catalytic tests, 0.6 g of fresh Zn/HZSM-5 (4.42 wt%) was treated at 700 °C for 30 min in the flow of helium, and then cooled down to 50 °C. When the temperature was kept at 50 °C, the mixed feed gas consisting of He 10%, CH₄ 45%, and CO 45% was introduced into the catalyst bed with a flow

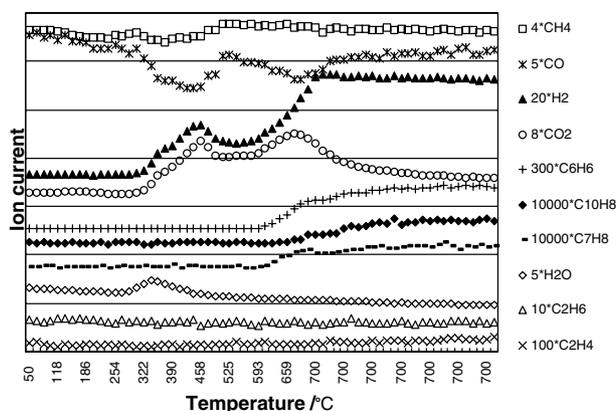


Fig. 2. Temperature-programmed coupling reaction over Zn/HZSM-5 as a function of reaction temperature.

rate of 18 ml/min. One hour later, the temperature was stepwise elevated to 700 °C at a heating rate of 10 °C/min, and kept isothermally for 1 h. An on-line MS monitored the composition of effluent.

The signal intensity of methane and CO has exhibited a clear decrease at about 370 °C, with the emergence of visible H₂O, H₂ and CO₂ signals (in Fig. 2), which further confirmed the essentiality of methane and CO for the formation of hydrocarbons over Zn/HZSM-5. The highest conversion of CO was realized at about 460 °C, without any detectable amount of ethylene, ethane, benzene and naphthalene. Since ZnO was very difficult to be reduced below 800 °C as proven by the TPR experiment, the redox reaction of methane with CO over the catalyst could be responsible for the formation of H₂, H₂O, CO₂, and reactive coke, which might be the initial product in the formation of hydrocarbons. When the reaction temperature was at 600 °C, the coupling reaction was efficiently initiated to yield CO₂, H₂ and aromatic products such as benzene, toluene and naphthalene. There was no visible change on the signal intensity of ethane and ethylene, even magnified 10,000 times.

The occurrence of this reaction was also validated in a conventional fixed-bed reactor and monitored by an on-line GC. Fig. 3 shows the conversion of methane and CO, and the selectivity of products after 5 h on stream at atmospheric pressure over 4.68% Zn/HZSM-5. The data in Fig. 3 further indicate that Zn/HZSM-5 was effective catalyst for the coupling methane with CO. The conversion is evident even at 500 °C, although the conversion of methane and the selectivity of aromatic products dropped sharply. When methane alone was introduced onto the freshly calcined catalysts at 500 °C, no products were detected, then the reactant gas was switched to the methane and CO mixture, small amount of aromatic products were formed after several

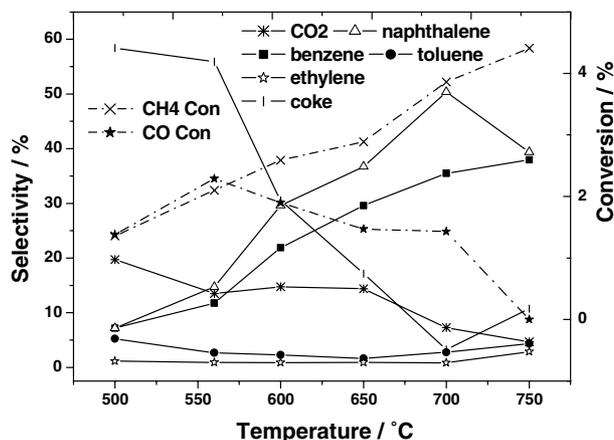


Fig. 3. Conversion of reactants and selectivity of products as a function of temperature for coupling CH₄ with CO over 4.68% Zn/HZSM-5 (Composition of feed gas: 36.40% methane, 61.94% CO and 1.66% He).

minutes induction period. In the case that only CO was introduced, no hydrocarbons are detected. These results indicate that both methane and CO are required for the products formation.

Increasing the reaction temperature causes a dramatic increase of the conversion of methane and the selectivity of benzene and naphthalene. The conversion of CO increased upon raising the temperature and went through a maximum at 550 °C then decreased. Coke formed heavily at the lower temperature then dropped sharply with the increasing temperature. Unlike the Mo/HZSM-5 catalyst that characterized by a higher selectivity to benzene and a less selectivity to naphthalene, the selectivity of naphthalene is higher than that of benzene under the investigated conditions. There is no clearly variety on the selectivity of ethylene and CO₂ in the case investigated. The optimum reaction temperature is about 700 °C.

4. Conclusions

The present work investigated high-throughput screening of HZSM-5 supported metal-oxides catalysts for the coupling of methane with CO to aromatics. The coupling reaction of methane with CO toward aromatics could be carried out over Zn/HZSM-5 even at the temperature as low as 500 °C, indicating that inert methane could be easily activated in the presence of CO at lower temperatures over the Zn/HZSM-5 catalyst. However, the conversion of reactants and the selectivity of benzene were appreciably lower than that of the traditional dehydroaromatization of methane over the Mo/HZSM-5 catalyst. The coexistence of methane and CO was found to be essential for the yield of aromatics over

Zn/HZSM-5. It was proposed that the reactive coke species formed on the catalyst might be the initial product in the formation of hydrocarbons.

Acknowledgments

We are most grateful to the financial support from BP Co. We thank Chinese Academy of Sciences (KGCX2-201-3) and “State 863 project” (2002AA321020) for partial funding of this research.

References

- [1] V.R. Choudhary, A.K. Kinage, T.V. Choudhary, *Science* 275 (1997) 1286.
- [2] T. Baba, H. Sawada, Y. Abe, Y. Ono, 13th International Zeolite Conference, France, July, 2000.
- [3] O.A. Anunziata, G.A. Eimer, L.B. Pierella, *Catal. Lett.* 58 (1999) 235.
- [4] S. Naito, T. Karaki, T. Iritani, *Chem. Lett.* (1997) 877.
- [5] S. Naito, T. Karaki, T. Iritani, M. Kumano, *Stud. Surf. Sci. Catal.* 119 (1998) 265.
- [6] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.* 21 (1993) 35.
- [7] Y. Xu, L. Lin, *Appl. Catal. A* 188 (1999) 53.
- [8] Y. Shu, M. Ichikawa, *Catal. Today* 71 (2001) 55.
- [9] Z. Liu, M.A. Nutt, E. Iglesia, *Catal. Lett.* 81 (2002) 271.
- [10] S. Liu, Q. Dong, R. Ohnishi, M. Ichikawa, *Chem. Commun.* (1998) 1217.
- [11] L. Wang, R. Ohnishi, M. Ichikawa, *J. Catal.* 190 (2000) 276.
- [12] R. Ohnishi, S. Liu, Q. Dong, L. Wang, M. Ichikawa, *J. Catal.* 182 (1999) 92.
- [13] Y. Xu, S. Liu, L. Wang, M. Xie, X. Guo, *Catal. Lett.* 30 (1995) 135.
- [14] H. Wang, Z. Liu, J. Shen, H. Liu, *Catal. Commun.* 5 (2004) 55.
- [15] H. Wang, Z. Liu, J. Shen, H. Liu, *J. Comb. Chem.* 5 (2003) 802.
- [16] S. Liu, Q. Dong, R. Ohnishi, M. Ichikawa, *Chem. Commun.* (1997) 1455.