

# Simultaneous conversion of methane and carbon dioxide to aromatics over silica supported chromium-based catalysts

Hui Zhang<sup>ab</sup> and Yuan Kou<sup>\*a</sup>

<sup>a</sup> College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.  
E-mail: yuankou@pku.edu.cn

<sup>b</sup> Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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## Simultaneous activation of methane and carbon dioxide to aromatics (SAMCA) over sodium-modified silica supported chromium-based catalysts is reported.

In this decade, much attention has been paid to the aromatization of methane under non-oxidative conditions following the early work conducted by Bragin *et al.*<sup>1</sup> Effective catalysts and mechanisms have been recently reviewed.<sup>2,3</sup> Molybdenum oxide supported on HZSM-5 zeolite seems to be a uniquely effective catalyst system for the aromatization of methane under non-oxidative conditions.<sup>2–6</sup> However, understanding the interaction of methane with the surfaces greatly depends upon various observations. It appears, in general, that reduction and/or carbidation of Mo species over Mo/ZSM-5 catalyst plays a key role in the activation of methane to produce initial C<sub>2</sub> products, and the primary intermediates are then further oligomerized to benzene on the B-acid sites within the channels of ZSM-5 zeolite.<sup>2,3,6</sup> Recently, we have found that sodium-modified silica supported chromium-based catalysts exhibit considerable activity for the simultaneous activation of methane and carbon dioxide to aromatics (SAMCA). This is the first investigation, to our knowledge, to use non-zeolite supported oxide catalysts for the non-free-oxygen activation of methane to produce benzene and toluene in the presence of large amounts of carbon dioxide.

The catalysts were prepared as follows. CR18, as a typical example, is described in detail. Given amounts of Cr<sub>2</sub>O<sub>3</sub> (0.35 g) and/or (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (the molar ratio of Cr<sub>2</sub>O<sub>3</sub> to (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is 2:1) and NaNO<sub>3</sub> (0.89 g) were slurred with silica sol (42 wt% water, 45 g) for 3 h, and then dried overnight at 120 °C. Several samples with different metal loadings and different Cr(III)/Cr(VI) ratios were prepared by controlling the concentration of the sol. The resulting samples were calcined at 500 °C for 4 h and then at 800 °C for 4 h. All of the calcined catalyst samples were crushed and sieved to 26–55 mesh. The XPS spectrum in the Cr 2p region for the catalyst CR18 revealed a strong peak at a binding energy of 579.0 eV and a shoulder of this peak at a binding energy of 576.6 eV corresponding to Cr(VI) 2p<sub>3/2</sub> and Cr(III) 2p<sub>3/2</sub>, respectively. The ratio of Cr(VI)/Cr(III) in CR18 on the basis of the XPS peak area is 5:1.

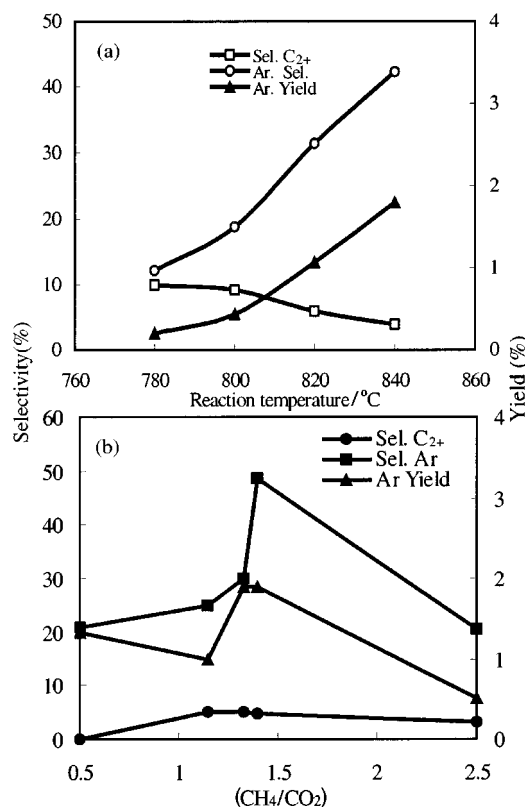
The catalytic runs were carried out at a pressure of 0.4 MPa in a fixed-bed vertical-flow stainless steel reactor mounted inside a tube furnace. The amount of the catalyst charged in the reactor was 1.0 g. The catalyst was pretreated in highly pure nitrogen (99.99%) at 840 °C for 30 min. Then, the reactant gas mixture (CH<sub>4</sub>:CO<sub>2</sub> = 7:5) was introduced at a flow rate of 22 ml min<sup>-1</sup>. When the support (SiO<sub>2</sub>) was used as a catalyst alone, the reaction results also indicated small amounts of aromatics (yield < 0.07%, see Table 1). Isotopic trace experiments were carried out under the same conditions but at a pressure of 0.3 MPa. Pure <sup>13</sup>CO<sub>2</sub> obtained from Ba<sup>13</sup>CO<sub>3</sub> was pressurized to 0.3 MPa by high pressure CH<sub>4</sub> and CO<sub>2</sub> to give a CH<sub>4</sub>/CO<sub>2</sub> molar ratio of 7/5. The relative partial pressure of <sup>13</sup>CO<sub>2</sub> in the CO<sub>2</sub> mixture was calculated to be 1/3.

The products in the effluent stream were analyzed by an online GC equipped with a Haysep Q column (TCD, H<sub>2</sub> as

carrier) for CO, CH<sub>4</sub>, CO<sub>2</sub> and C<sub>1</sub>–C<sub>3</sub>, 13X and 5A sieve columns (TCD, Argon as carrier) for H<sub>2</sub>, CH<sub>4</sub> and CO, and a quartz capillary column coated with SE-54 (FID) for benzene and toluene. Both methane and carbon dioxide were 99.995% pure.

Operating parameters significantly influence the activity of the catalyst in the SAMCA reaction. Fig. 1(a) shows that both the aromatics yield and the selectivity are increased by increasing the reaction temperature. The yield and the selectivity of aromatics are also found to go through maxima at a contact time of 0.79 h g l<sup>-1</sup>, indicating that deep oxidation may occur when the contact time is > 0.79 h g l<sup>-1</sup>.

Fig. 1(b) shows the effect of the CH<sub>4</sub>/CO<sub>2</sub> molar ratio on the selectivities and the yields at 840 °C. Both the selectivity and the yield of aromatics are enhanced with an increasing proportion of CH<sub>4</sub> in the reactant mixture, and reach a maximum at a CH<sub>4</sub>/CO<sub>2</sub> molar ratio of 1.4. However, the selectivity to C<sub>2+</sub> hydrocarbons essentially remains constant for CH<sub>4</sub>/CO<sub>2</sub> molar ratios of > 1.1. When the molar ratio of CH<sub>4</sub>/CO<sub>2</sub> is < 0.5 or > 2.5, both C<sub>2+</sub> hydrocarbons and aromatics are difficult to detect. It is of note that the yields of C<sub>2+</sub>



**Fig. 1** Effect of operating parameters on the activity of the catalyst 5 wt% Na–7.5 wt% Cr/SiO<sub>2</sub> in SAMCA. (a) Effect of reaction temperature (0.4 MPa, 0.79 h g l<sup>-1</sup>, CH<sub>4</sub>/CO<sub>2</sub> = 7:5) and (b) effect of CH<sub>4</sub>/CO<sub>2</sub> molar ratio (0.4 MPa, 0.79 h g l<sup>-1</sup>, 840 °C).

**Table 1** Catalytic performances of a series of chromium-based catalysts in the SAMCA reaction<sup>a</sup>

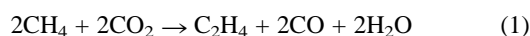
Catalyst	Cr (wt%)	Na (wt%)	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>	V/cm <sup>3</sup> g <sup>-1</sup>	Conversion		Selectivity			Aromatics yield (%)
					CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> <sup>+</sup>	Ar <sup>b</sup>	CO	
SiO <sub>2</sub>	0	0	204.48	46.8	0.9	5.1	11.9	7.6	80.4	0.07
CR16	7.5	0	202.44	46.17	2.7	21.4	0.0	23.7	76.3	0.6
CR17	7.5	2	10.05	2.29	2.4	10.6	4.1	38.4	57.5	0.9
CR18	7.5	5	3.35	0.76	3.8	16.0	4.8	48.7	46.5	1.9
CR19	7.5	10	1.87	0.43	4.0	7.1	4.1	41.2	54.7	1.7
CR7 <sup>c</sup>	11.4	2	9.80	2.11	1.4	13.5	3.6	1.8	94.6	0.03
CR8 <sup>d</sup>	8.9	2	10.12	2.19	2.3	16.6	4.0	30.7	65.3	0.7
CR15 <sup>e</sup>	7.5	10	2.11	0.51	1.9		30.5	5.2	64.2	0.1
CR10 <sup>e</sup>	7.5	2	9.51	2.13	2.1		23.1	2.2	74.7	0.05

<sup>a</sup> Reaction conditions: 0.4 MPa, 840 °C, 20–23 ml min<sup>-1</sup>, CH<sub>4</sub>/CO<sub>2</sub> = 7/5. <sup>b</sup> Benzene + toluene. <sup>c</sup> Na–Cr(III)/SiO<sub>2</sub>. <sup>d</sup> Na–Cr(VI)/SiO<sub>2</sub>. <sup>e</sup> CH<sub>4</sub> feed only.

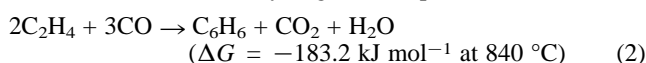
hydrocarbons and aromatics are very low when only methane is fed into the reaction mixture as demonstrated by the results for CR10 and CR15 in Table 1.

Variation of the Cr<sup>3+</sup>/Cr<sup>6+</sup> ratio in the preparation of the catalyst precursors has a considerable effect on the activity of the catalyst in SAMCA. The reaction results obtained from a series of chromium-based catalysts are presented in Table 1. Over the Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst (CR7 in Table 1), the dominant product is carbon monoxide (94.6%) although C<sub>2</sub><sup>+</sup> and aromatics are detectable. This situation is very similar to the results over a Cr<sub>2</sub>O<sub>3</sub> catalyst reported by Asami *et al.*<sup>7</sup> except that they observed no aromatics.<sup>7</sup> However, addition of Cr<sup>VI</sup> to the Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst led to significantly increased SAMCA reactivity. In particular, over the catalyst containing a 2:1 molar ratio of Cr<sup>3+</sup> to Cr<sup>6+</sup> and modified with 5 wt% sodium promoter (CR18), CH<sub>4</sub> conversion reaches 3.8%, while selectivity to aromatics increases to 48.7%. By comparison, when only Cr<sup>VI</sup> species are present on the fresh catalyst surface (CR8), the CH<sub>4</sub> conversion decreases to 2.6%, and the selectivity to aromatics also decreased to 13.9%. Interestingly, when the highest selectivity to aromatics is obtained over CR18 (5 wt% Na and 2:1 molar ratio of Cr<sup>3+</sup> to Cr<sup>6+</sup>), the selectivity to CO is at a minimum, and the molar ratio of benzene to CO is ca. 1:1. In this case, small amounts of H<sub>2</sub> were observed at a CO/H<sub>2</sub> molar ratio of 3. However, after being on-stream for 6 h, the catalyst CR18 shows behavior more closely resembling that of Cr<sub>2</sub>O<sub>3</sub> (CR7). Correspondingly, XPS analysis of the quenched catalyst indicates the Cr(III) 2p<sub>3/2</sub> peak only. As proposed previously,<sup>8–10</sup> it is highly probable that mixing of octahedral and tetrahedral site-symmetries on the surface of the supported oxide catalyst presents catalytically active sites for the SAMCA reaction.

Asami *et al.* have proposed the reaction given by eqn. (1) to explain the formation of ethene:<sup>7</sup>

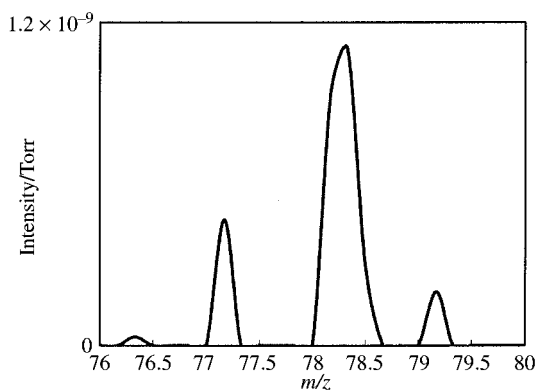


We tentatively suggest a subsequent additional step here to explain the formation of benzene for SAMCA in which the CO molecules can be obtained from either reaction (1) or the partial reduction of CO<sub>2</sub> in the hydrogen atmosphere.



In order to confirm whether CO<sub>2</sub> participates in the formation of benzene, isotopic trace experiments using <sup>13</sup>CO<sub>2</sub> in CH<sub>4</sub> and CO<sub>2</sub> co-feed have been carried out under a pressure of 0.3 MPa. The <sup>13</sup>CC<sub>5</sub>H<sub>6</sub> species, which was not observed by using the normal CH<sub>4</sub>–CO<sub>2</sub> mixture as the feed gas, is identified by a peak at *m/z* 79.17 in the online mass spectrum (Fig. 2), indicating that the carbon in CO<sub>2</sub> demonstrably takes part in the construction of the benzene ring.

Despite their low reactivity, this work has demonstrated that methane and carbon dioxide can be simultaneously activated. The reaction producing aromatics over silica supported chromium-based catalysts is accompanied by an induction period of ca. 20 minutes. Ethene, as the primary intermediate, is



**Fig. 2** MS spectra of the products formed in the SAMCA reaction with <sup>13</sup>CO<sub>2</sub>-labelled reactant.

necessary for the formation of benzene, however, the definite requirement of zeolite channels as proposed based on the Mo/ZSM-5 system is questioned. This research may therefore lead to some new insights on the mechanism for the aromatization of methane.

Further work is in progress, not only to carry out the reaction on a larger experimental scale, but also to elucidate the nature of the mixed site-symmetry/oxidation state catalysts by XAFS analysis.

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## Notes and references

- 1 A. V. Bragin, T. V. Vasina, A. V. Preobrazhenskii and K. M. Minachev, *IZV. Akad. Nauk. SSSR Ser. Khim.*, 1989, **3**, 750.
- 2 D. Wang, M. Rosynek and J. H. Lunsford, *J. Catal.*, 1997, **169**, 347.
- 3 J. Zhang, M. Long and R. Howe, *Catal. Today*, 1998, **44**, 293.
- 4 Y. Xu, S. Liu, L. Wang, M. Xie and X. Guo, *Catal. Lett.*, 1995, **30**, 135.
- 5 L. Chen, L. Lin, Z. Xu, X. Li and T. Zhang, *J. Catal.*, 1995, **157**, 190.
- 6 Y. Shu, Y. Xu, S. Wong, L. Wang and X. Guo, *J. Catal.*, 1997, **170**, 11.
- 7 K. Asami, T. Fujita, K. I. Kusakabe, Y. Nishiyama and Y. Ohtsaka, *Appl. Catal. A*, 1995, **126**, 245.
- 8 H. Zhang, J. Niu and Y. Kou, T. Tanaka and S. Yoshida, *J. Solid State Chem.*, 1998, **137**, 325.
- 9 Y. Kou and H. Wang, *5th China–Japan Bilateral Symposium on Effective Utilization of Carbon Resources (EUCR-V) Proceedings*, Chengdu, China, 1997, p. 5.
- 10 H. Zhang and Y. Kou, *5th China–Japan Bilateral Symposium on Effective Utilization of Carbon Resources (EUCR-V) Proceedings*, Chengdu, China, 1997, p. 137.