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# Conversion of methane to C<sub>2</sub> and C<sub>3</sub> hydrocarbons over TiO<sub>2</sub>/ZSM-5 core-shell particles in an electric field†

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Catalytic conversion of methane (CH<sub>4</sub>) to light olefins is motivated by increasing recoverable reserves of methane resources, abundantly available in natural gas, shale gas, and gas hydrates. The development of effective processes for conversion of CH<sub>4</sub> to light olefins is still a great challenge. The interface of ZSM-5 zeolite and TiO<sub>2</sub> nanoparticles is successfully constructed in their core-shell particles via mechanochemical treatment with high shear stress. The oxidative coupling of methane at a low temperature under application of an electric field may be induced by the O<sub>2</sub> activation via electrons running through the surface of TiO<sub>2</sub> located at the interface of TiO<sub>2</sub> and zeolite particles. Moreover, C<sub>3</sub>H<sub>6</sub> was also produced by the ethylene to propylene (ETP) reaction catalyzed by Brønsted acid sites in the ZSM-5 zeolite within core-shell particles.

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## 1. Introduction

Proven reserves of natural gas have significantly increased in the last decade mainly due to the exploitation of unconventional natural gas sources such as shale gas, coal-bed methane and gas hydrates.<sup>1</sup> Methane (CH<sub>4</sub>), the principal component of natural gas, has been proposed as an alternative feedstock to petroleum for the production of high value-added chemicals as well as an energy resource. Methane can be conventionally converted through syngas (a mixture of CO and H<sub>2</sub>) as an intermediate<sup>2-5</sup> to high value-added chemicals such as methanol, light olefins, and aromatics; however, this indirect route consumes a large quantity of external energy to produce syngas.<sup>5</sup> The development of energy-saving processes for the direct conversion of methane to high value-added chemicals thus remains a significant challenge.

Oxidative coupling of methane (OCM) is an efficient technology that directly converts CH<sub>4</sub> to C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. Since Keller and Bhasin proposed this process in the 1980s,<sup>6</sup> Hinsen and Baerns,<sup>7</sup> Ito and Lunsford,<sup>8</sup> and many other groups have reported various OCM catalysts.<sup>9-13</sup> A database of high-performance OCM catalysts was reviewed by Zavyalova and co-

workers.<sup>14</sup> For most of the catalysts listed in this review, a high reaction temperature over 700 °C is necessary to realize OCM; however, this can promote the over-oxidation of reaction intermediates to CO and CO<sub>2</sub>, so that the yield of desirable products, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>, is limited.<sup>14</sup>

The formation of methyl radicals from CH<sub>4</sub> has a high activation energy due to the high H-CH<sub>3</sub> bond dissociation energy (435 kJ mol<sup>-1</sup>).<sup>15</sup> On the other hand, a low reaction temperature is favorable for the selective production of desirable products (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>), due to the suppression of deeper catalytic oxidation and non-catalytic gas-phase oxidation of reaction intermediates. To overcome these issues, non-equilibrium plasma has been proposed as a promising technology to realize high electron temperatures under low gas-phase temperatures.<sup>16</sup> Non-oxidative coupling of CH<sub>4</sub> in non-equilibrium plasma reaction systems such as corona discharge<sup>16,17</sup> and spark discharge<sup>18,19</sup> have been widely investigated. Liu *et al.*<sup>16,17</sup> utilized corona discharge with zeolite catalysts to produce higher hydrocarbons; C<sub>2</sub> hydrocarbons (mostly C<sub>2</sub>H<sub>2</sub>), and trace C<sub>3</sub><sup>+</sup> hydrocarbons were obtained with an input power of 9 W (input voltage, 7 kV) in this reaction system. Kado *et al.*<sup>18</sup> reported the non-catalytic direct conversion of CH<sub>4</sub> to C<sub>2</sub>H<sub>2</sub> using corona discharge. This process can also produce a large amount of C<sub>2</sub>H<sub>2</sub> (49% yield) with a supplied power of approximately 50 W. However, a great deal of carbon deposition occurred on the electrodes during reaction. Spark discharge was also applied for producing C<sub>2</sub>H<sub>2</sub> from CH<sub>4</sub>.<sup>19</sup> High selectivity toward C<sub>2</sub>H<sub>2</sub> (>85%) and lesser amounts of deposited carbon were achieved. Furthermore, the energy efficiency with spark discharge was much higher (12.1 kW h (kg-C<sub>2</sub>H<sub>2</sub>)<sup>-1</sup>) than that in dielectric barrier discharge (DBD) or corona discharge.<sup>19</sup> Liu

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*et al.*<sup>20–22</sup> also reported the direct conversion of CH<sub>4</sub> and CO<sub>2</sub> to higher hydrocarbons *via* DBD with zeolite catalysts. The products in this reaction system included syngas (CO + H<sub>2</sub>), light hydrocarbons (C<sub>2</sub> and C<sub>3</sub>), liquid hydrocarbons (C<sub>4</sub><sup>+</sup>), plasma-polymerized film, and carbon oxides (CO and CO<sub>2</sub>).<sup>21</sup> The selectivity toward CO and C<sub>4</sub><sup>+</sup> was greater than 80%; however, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> yields were extremely low (1.2% and 2.1%, respectively) with an applied power of 500 W.<sup>22</sup>

As an alternative, OCM can be achieved by application of a direct current (DC) to the semiconductive Sr-doped La<sub>2</sub>O<sub>3</sub> catalyst without excessive electric discharge.<sup>23</sup> Sekine and co-workers recently reported a Ce–W–O catalyst derived from CeO<sub>2</sub> modified with Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> polyoxometalate, which exhibited high OCM activity due to a synergetic effect between the Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> structure and the electric field to produce the reactive oxygen species for the selective oxidation of CH<sub>4</sub>.<sup>24–26</sup> The CePO<sub>4</sub> nanorods with uniform surface Ce sites could work as a durable catalyst and showed the highest C<sub>2</sub> yield of 18% in an electric field without the need for external heating.<sup>27</sup> More recently, McEwen and co-workers have reviewed some of the theoretical methods that have been used to elucidate the influence of external electric fields on catalytic reactions, as well as the application of such methods to selective methane activation.<sup>28</sup>

It is well-known that oxygen vacancies existing in the surface and bulk of TiO<sub>2</sub> (ref. 29–31) affect the catalytic activity in both the photoreactions and non-photoreactions.<sup>32,33</sup> The <sup>18</sup>O isotopic exchange reaction on metal oxide catalysts is a convincing method for revealing the existence of the activated oxygen species on the surface of catalyst to progress the OCM reaction. Miradatos and co-workers<sup>34</sup> have investigated the elementary steps dealing with the oxygen and methane activation in the OCM over lanthanum oxide catalyst using isotope transient experiments using <sup>18</sup>O<sub>2</sub>. They suggest that the fast interaction between gaseous oxygen and lattice oxygen atoms, involving the formation of active oxygen species possible to dissociate C–H bonds, could be considered for most of the performing systems at higher reaction temperature. More recently, Ogo and co-workers have conducted the <sup>18</sup>O<sub>2</sub> isotope experiments and suggest that mobile oxygen over La<sub>1–x</sub>Ca<sub>x</sub>AlO<sub>3–δ</sub> perovskite catalysts in an electric field promotes low-temperature OCM reaction.<sup>35</sup>

Zeolites are widely applied as a component of catalysts for the direct conversion of CH<sub>4</sub> to CH<sub>3</sub>OH and for the methane dehydroaromatization (MDA) reaction due to their ion exchange ability, unique pore structure, and acid-catalytic properties. Cu-based zeolites<sup>36–38</sup> and iron-containing zeolites<sup>38–40</sup> have recently been studied for their potential in the selective oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH under oxidative conditions at low temperature. Under non-oxidative conditions, Zn,<sup>41</sup> Mo,<sup>41–44</sup> Mn,<sup>45</sup> and Fe<sup>45</sup> dispersed on zeolites have exhibited excellent catalytic performance for the MDA reaction.

In the present study, we tried to promote that the O<sub>2</sub> activation *via* electrons running through the surface of TiO<sub>2</sub> located at the interface of TiO<sub>2</sub> and zeolite particles induces the OCM reaction at a lower temperature under application of an electric field. Mechanochemical treatment using a powder composer with high shear stress<sup>46</sup> was employed to prepare this characteristic catalyst with a core–shell structure, where microsized

zeolite cores and nanosized TiO<sub>2</sub> shells form particles. ZSM-5 zeolite (MFI topology) with intersectional 10–10-ring channel system was selected to form the core of the particles because it has been most widely industrialized as a solid-acid catalyst for the selective production of light olefins.<sup>47–51</sup> Moreover, the ZSM-5 catalyst has exhibited high yield in the ethylene to propylene (ETP) reaction.<sup>52,53</sup> Therefore, the production of C<sub>2</sub> hydrocarbons as well as the selective production of C<sub>3</sub>H<sub>6</sub> is expected using this type of catalyst with a core–shell structure because of C<sub>2</sub>H<sub>4</sub> produced *via* OCM in an electric field can be catalytically converted to C<sub>3</sub>H<sub>6</sub> by the ETP reaction on the Brønsted acid sites of ZSM-5 within the core–shell particles.

## 2. Experimental

### 2.1. Catalyst preparation

TiO<sub>2</sub> nanoparticles used in this study were commercially available from Aldrich. ZSM-5 zeolite (MFI topology, Si/Al = 16, JGC Catalysts and Chemicals Ltd.) was used in this study. Silicalite-1, which is a pure-silica version of MFI-type zeolite, was hydrothermally synthesized using tetrapropylammonium bromide as a structure-directing agent (see ESI† for the detailed synthetic procedure).

The zeolite–TiO<sub>2</sub> core–shell particles were mechanochemically prepared by the application of high shear stress using a high-performance powder processing machine (Nobilta NOB-mini, Hosokawa Micron Corporation). We have already confirmed that the crystallinity and microporosity of the single ZSM-5 zeolite were retained during this kind of mechanochemical treatment.<sup>54</sup> The mechanochemical treatment was typically performed as follows: after a portion of TiO<sub>2</sub> nanoparticles (1.2 g) was added to ZSM-5 (6.0 g), mechanochemical treatment was performed at 1000 rpm for 5 min, and then at 9000 rpm for 10 min. Another portion of TiO<sub>2</sub> nanoparticles (1.2 g) was then added to the treated mixture, which was mechanochemically treated using the same procedure. These procedures were repeated three more times until the weight of added TiO<sub>2</sub> was equal to that of ZSM-5. The time-courses of rotational speed and the resulting output power are shown in Fig. S1.† The obtained sample is designated as TiO<sub>2</sub>(mc)/ZSM-5. For comparison, the core–shell particles of silicalite-1 (MFI topology) and TiO<sub>2</sub> were also prepared according to the same procedure, and the prepared samples is designated as TiO<sub>2</sub>(mc)/silicalite-1. A physical mixture of TiO<sub>2</sub> and ZSM-5 with the same weights was prepared and is designated as TiO<sub>2</sub>(pm)/ZSM-5. The prepared core–shell particles, the physical mixture, and the simple TiO<sub>2</sub> or ZSM-5 were calcined at 800 °C for 12 h in a muffle furnace (denoted 800 in the end of sample name; *i.e.*, ZSM-5\_800).

### 2.2. Characterization of catalysts

The prepared samples were measured using power X-ray diffraction (XRD, Ultima-IV, Rigaku) with Cu K $\alpha$  radiation at 40 kV and 20 mA to confirm the crystallinity and phase purity. The shape and particle size of the samples were observed using field emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL). Cross-sectional observation of the core–shell particles and their EDS line-



scanning and mapping were performed using another FE-SEM (SU9000, Hitachi High-Technologies) equipped with energy dispersive X-ray spectroscopy (EDS; Genesis, EDAX), which was measured at an accelerating voltage of 5.0 kV. Nitrogen adsorption and desorption isotherms were collected at  $-196\text{ }^{\circ}\text{C}$  with an Autosorb-iQ analyzer (Quantachrome Instruments). Prior to measurement, each sample was heated *in vacuo* (less than 10 Pa) at  $400\text{ }^{\circ}\text{C}$  for 12 h. The specific surface area ( $S_{\text{BET}}$ ) and micropore volume ( $V_{\text{micro}}$ ) were estimated using the Brunauer-Emmett-Teller (BET) and *t*-plot methods, respectively. The chemical composition (Si/Al molar ratio) of the zeolites was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ICPE-9000, Shimadzu). The number of acid sites was measured by ammonia temperature-programmed desorption ( $\text{NH}_3$ -TPD) measurement on a BELCAT-B (MicrotracBEL Corp.) with a thermal conductivity detector (TCD). The catalyst was preheated at  $600\text{ }^{\circ}\text{C}$  prior to the measurement under He flow. The TPD data were collected at a ramping rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . The number of acid sites was determined from the area of h-peak<sup>55–57</sup> in their profiles. Coke deposition on the used catalyst was evaluated using thermogravimetric analysis (TGA, TG-8120, Rigaku) at a ramping rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from room temperature to  $800\text{ }^{\circ}\text{C}$  under air flow ( $30\text{ cm}^3\text{ (SATP) min}^{-1}$ ).

### 2.3. Activity test on the ethylene-to-propylene (ETP) reaction

The catalyst was pelletized to achieve a size of 355–500  $\mu\text{m}$ . The catalyst pellets were placed in a quartz tube (9.0 mm i.d.) as a fixed-bed reactor. Prior to the reaction, the catalyst was treated at  $550\text{ }^{\circ}\text{C}$  for 1 h under air flow ( $30\text{ cm}^3\text{ (SATP) min}^{-1}$ ). After the pretreatment, the gas flow was changed from air to He ( $30\text{ cm}^3\text{ (SATP) min}^{-1}$ ) followed by cooling to  $400\text{ }^{\circ}\text{C}$  or the other specified reaction temperature. The ETP reaction was performed at three different temperatures: 400, 450, and  $500\text{ }^{\circ}\text{C}$ . Ethylene ( $W_{\text{zeolite}}/F_{\text{ethylene}} = 16.4\text{ g-cat. h mol}^{-1}$ ) was introduced into the top of the catalyst-bed with He as a carrier gas ( $30\text{ cm}^3\text{ (SATP) min}^{-1}$ ). The  $\text{C}_2\text{H}_4$  and products were analyzed using an online gas-chromatograph with flame ionization detector (GC-FID; GC-2014, Shimadzu) equipped with a DB-5 capillary column (60 m length; 0.53 mm i.d.; 5.0  $\mu\text{m}$  thick) and an offline GC-FID (GC-2014, Shimadzu) with a KCl/ $\text{Al}_2\text{O}_3$  capillary column (50 m length; 0.53 mm i.d.; 10  $\mu\text{m}$  thick). The conversion of  $\text{C}_2\text{H}_4$ , the yield and distribution of products, and the material balance were calculated on the carbon-basis of the input amount of  $\text{C}_2\text{H}_4$ .

### 2.4. Activity test on OCM reaction in an electric field

The catalytic performance of each prepared catalyst for the OCM reaction was tested with a fixed-bed continuous-flow reactor, of which a schematic image is presented in Fig. S2.† The catalyst was pelletized without any binder, roughly crushed and then sieved to obtain catalyst pellets with 355–500  $\mu\text{m}$  in size. The catalyst pellets (100 mg) were charged into a quartz tube (4.0 mm i.d.) as a continuous-flow reactor. When the reaction was conducted with application of a voltage in the catalyst bed, two stainless-steel electrodes (2.0 mm i.d.) were separately set in the reactor without contact with each other; one electrode contacted with the upper side of the catalyst bed,

and the other contacted the lower side. The voltage in the catalyst-bed was applied under constant-current conditions using a DC power supply (HAR-30N40, Matsusada Precision Inc.). The supplied current was controlled from 2.0 to 9.0 mA to make the electric field stable. Time courses of the input current and the resulting voltage were recorded using an oscilloscope (TDS 3052B, Tektronix). Prior to the reaction, the catalyst bed was heated at  $300\text{ }^{\circ}\text{C}$  using a furnace for 30 min under Ar flow ( $60\text{ cm}^3\text{ (SATP) min}^{-1}$ ). After cooling the furnace to  $150\text{ }^{\circ}\text{C}$ , the reactants ( $\text{CH}_4$  and  $\text{O}_2$ ) and carrier gas (Ar) were fed into the reactor ( $\text{CH}_4:\text{O}_2:\text{Ar} = 25:15:60\text{ cm}^3\text{ (SATP) min}^{-1}$ ,  $W/F_{\text{methane}} = 1.6\text{ g-cat. h mol}^{-1}$ ). The temperature at the lower side of the catalyst-bed was monitored using a K-type sheathed thermocouple. The products after passing a cold trap were analyzed using a gas chromatograph with a thermal conductivity detector (GC-TCD; GC-8A, Shimadzu) and two GC-FIDs (GC-2014, Shimadzu). The GC-TCD was equipped with a molecular sieve 5A packed column (2.0 m length; 3.0 mm i.d.). One GC-FID was equipped with a Porapak N packed column (4.0 m length; 3.0 mm i.d.) and a methanizer (Ru/ $\text{Al}_2\text{O}_3$  catalyst), while the other had a KCl/ $\text{Al}_2\text{O}_3$  capillary column (50 m length; 0.53 mm i.d.; 10  $\mu\text{m}$  thick).

The conversion of  $\text{CH}_4$  and  $\text{O}_2$ , product yield, and product selectivity were determined by the following eqn (1)–(4):

$$\text{CH}_4\text{ conversion (\%)} = \left\{ \frac{\text{sum of C-atom moles of each product}}{\text{C-atom moles of input CH}_4} \right\} \times 100 \quad (1)$$

$$\text{O}_2\text{ conversion (\%)} = \left\{ \frac{\text{moles of O}_2\text{ consumed}}{\text{moles of input O}_2} \right\} \times 100 \quad (2)$$

$$\text{Product yield (C\%)} = \left\{ \frac{\text{C-atom moles of each product}}{\text{C-atom moles of input CH}_4} \right\} \quad (3)$$

$$\text{Product selectivity (C\%)} = \left\{ \frac{\text{product yield}}{\text{CH}_4\text{ conversion}} \right\} \times 100 \quad (4)$$

Since reliable material balance is always achieved in the range from low to high  $\text{CH}_4$  conversion which is based on the appearance of carbon-containing products (hydrocarbons and  $\text{CO}/\text{CO}_2$ ), the  $\text{CH}_4$  conversion is estimated by the eqn (1).

When the reaction was conducted without application of a voltage in the catalyst bed, the catalyst was heated at prescribed temperatures (from 150 to  $900\text{ }^{\circ}\text{C}$ ) using a furnace and the same reaction conditions described above.

The  $^{16}\text{O}_2/^{18}\text{O}_2$  isotopic oxygen exchange experiment at  $150\text{ }^{\circ}\text{C}$  in an electric field was conducted. The details of experimental procedures were described in ESI.†

## 3. Result and discussion

### 3.1. Catalyst characterization

Three kinds of composed catalysts,  $\text{TiO}_2(\text{mc})/\text{ZSM-5}$ ,  $\text{TiO}_2(\text{mc})/\text{silicalite-1}$ , and  $\text{TiO}_2(\text{pm})/\text{ZSM-5}$ , were prepared in this study. Fig. 1 and S3† show XRD patterns of the samples before and after thermal treatment at  $800\text{ }^{\circ}\text{C}$ . The XRD patterns of as-received and calcined ZSM-5 showed only the MFI phase





without any impurities. The as-received  $\text{TiO}_2$  consisted of two crystalline polymorphs, anatase ( $P4_2/mnm$ ) and rutile ( $I4_1/amd$ ), whereas calcined  $\text{TiO}_2$  was only the rutile phase. This is a good consistency with a well-known phase transformation from anatase to rutile between 600 and 700 °C under atmospheric pressure.<sup>58–60</sup>

In the physical mixture of  $\text{TiO}_2$  and ZSM-5, the peak intensities corresponding to an MFI structure were reasonably decreased due to the weight ratio of  $\text{TiO}_2$  to ZSM-5. In contrast, mechanochemical treatment led to a decrease in the peak intensities of both  $\text{TiO}_2$  polymorphs, although those of MFI were almost unchanged. This indicates that high shear stress during mechanochemical treatment may cause partial amorphization of  $\text{TiO}_2$  nanoparticles.<sup>54</sup> With regard to the phase transformation of  $\text{TiO}_2$  during thermal treatment at 800 °C,  $\text{TiO}_2$  in  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$  was still composed of both anatase and rutile, while that in  $\text{TiO}_2(\text{pm})/\text{ZSM-5}_{800}$  was only rutile. There are numerous reports describing that  $\text{SiO}_2$  or several metal oxides act as an inhibitor to the phase transformation into rutile;<sup>61–64</sup> in particular,  $\text{SiO}_2$  species on the surface of  $\text{TiO}_2$  anatase induce a delay in the nucleation of  $\text{TiO}_2$  rutile.<sup>60,61</sup> It is thus supposed that strong adhesion of  $\text{TiO}_2$  nanoparticles on the surface of ZSM-5 particles occurs during mechanochemical treatment.

Fig. 2 shows FE-SEM images of  $\text{TiO}_2(\text{pm})/\text{ZSM-5}$  and  $\text{TiO}_2(\text{mc})/\text{ZSM-5}$  before and after thermal treatment at 800 °C. Typical FE-SEM images of  $\text{TiO}_2$  nanoparticles and the parent ZSM-5 zeolite particles are shown in Fig. S4.† The particle size of parent ZSM-5 was 1.5–2.0  $\mu\text{m}$  (Fig. S4b†). There were no significant differences in the morphologies of parent ZSM-5 and ZSM-5<sub>800</sub> (Fig. S4b and d†). On the other hand, the particle size of  $\text{TiO}_2$  was significantly increased from 25 to 100 nm by thermal treatment at 800 °C (Fig. S4a and c†). This is consistent with the sharpening of the XRD peaks that correspond to the  $\text{TiO}_2$  rutile polymorph.

It was evident that  $\text{TiO}_2(\text{pm})/\text{ZSM-5}_{800}$  consists of ZSM-5 zeolite particles and aggregates of  $\text{TiO}_2$  nanoparticles without good contact with each other (Fig. 2b). The surface of the ZSM-5 particles in  $\text{TiO}_2(\text{pm})/\text{ZSM-5}_{800}$  was still smooth (Fig. 2c), and similar to those of ZSM-5<sub>800</sub> (Fig. S4d†). In contrast, the

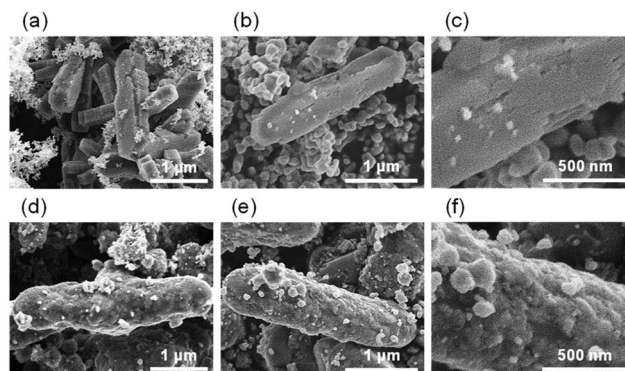


Fig. 2 FE-SEM images of (a)  $\text{TiO}_2(\text{pm})/\text{ZSM-5}$  and (d)  $\text{TiO}_2(\text{mc})/\text{ZSM-5}$ . (b) Low and (c) high magnification views of  $\text{TiO}_2(\text{pm})/\text{ZSM-5}_{800}$ . (e) Low and (f) high magnification views of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$ .

surface of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$  particles (Fig. 2e) was quite different from those of the parent ZSM-5 (Fig. S4b†); the former became rough (Fig. 2f) and the corners and edges of each composed particle became rounded (Fig. 2e), which indicates that the parent ZSM-5 particles were fully covered with a thin layer of  $\text{TiO}_2$  nanoparticles to give a core-shell structure. The same morphology was also observed in  $\text{TiO}_2(\text{mc})/\text{silicalite-1}_{800}$  (Fig. S5c and d†).

To further verify the distribution of  $\text{TiO}_2$  within the composed particles, EDS line-scanning and EDS-mapping of core-shell particle ( $\text{TiO}_2(\text{mc})/\text{ZSM-5}$ ) cross-section were performed. For line-scanning (Fig. 3b), the outer layer of the particle, which is the brightest region in the secondary electron image (Fig. 3a), is mainly composed of Ti atoms within  $\text{TiO}_2$ , while the core, the central part of the slender particle, consists of Si and Al atoms, which corresponds to ZSM-5 aluminosilicates. This indicates that

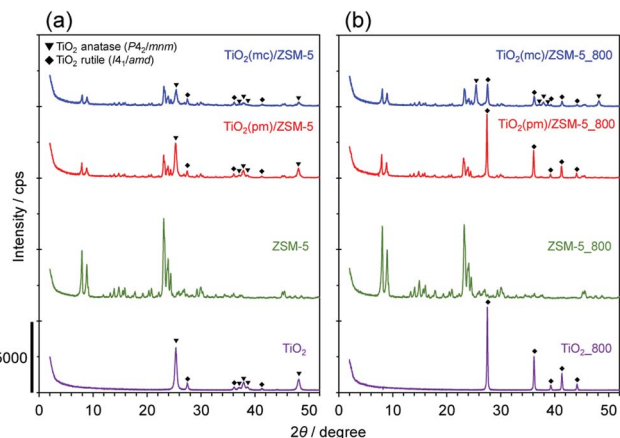


Fig. 1 Powder XRD patterns of (a) pristine and (b) thermally-treated samples at 800 °C.

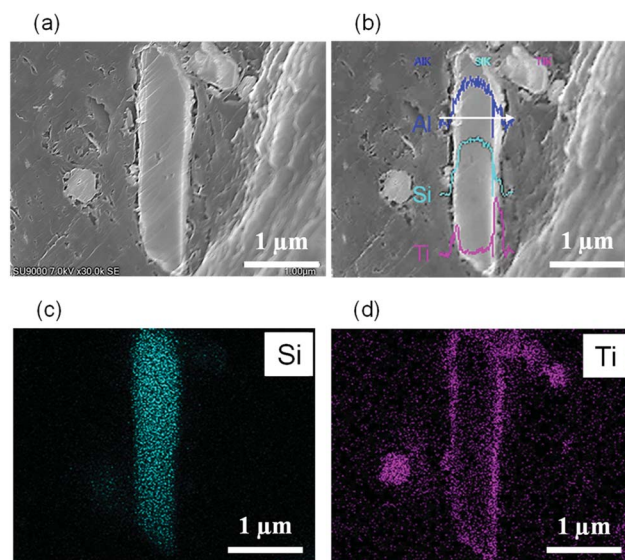


Fig. 3 SEM, EDS line-scanning and EDS-mapping images of the cross-section of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$ . (a) Secondary electron image, (b) EDS line-scanning of Si, Al and Ti, and mapping images of (c) Si and (d) Ti.



the prepared particles have a core-shell structure of ZSM-5 covered with a thin TiO<sub>2</sub> layer. The EDS-mapping (Fig. 3c and d) revealed the core-shell structure more clearly.

Table 1 lists the BET surface areas and micropore volumes of samples estimated from N<sub>2</sub> adsorption-desorption isotherms (see also Fig. S6†). After the thermal treatment, the BET surface area and micropore volume slightly decreased, probably due to dealumination from the MFI framework. This consideration is supported by the lack of damage in the microporous structure of silicalite-1, because there were no changes in BET surface area and micropore volume during thermal treatment. All the composite samples of 50 wt% TiO<sub>2</sub> and 50 wt% ZSM-5 exhibited reasonably smaller BET surface areas and micropore volumes; *i.e.*, the BET surface area (197 m<sup>2</sup> (g-bulk)<sup>-1</sup>) of TiO<sub>2</sub>(mc)/ZSM-5 was almost half of that (399 m<sup>2</sup> (g-bulk)<sup>-1</sup>) of the single ZSM-5. During both mechanochemical treatment and subsequent thermal treatment, it is revealed from retaining the micropore volumes corresponding to ZSM-5 zeolites within the core-shell particles (see Table 1) were unchanged.

It was concluded that the core-shell particles of TiO<sub>2</sub>(mc)/ZSM-5 were successfully prepared by mechanochemical treatment with high shear stress, without damage to the crystallinity.<sup>34</sup> In these core-shell particles, small molecules (*i.e.*, N<sub>2</sub>) can diffuse through the voids within the thin TiO<sub>2</sub> layer into the micropores of ZSM-5.

The acidic nature of TiO<sub>2</sub>(mc)/ZSM-5\_800 was evaluated by NH<sub>3</sub>-TPD measurements (see Fig. S7†). Based on the h-peak area in the NH<sub>3</sub>-TPD profile, the amount of acid sites of TiO<sub>2</sub>(mc)/ZSM-5\_800 (0.24 mmol (g-zeolite)<sup>-1</sup>) was almost the same as that of ZSM-5\_800 (0.25 mmol (g-zeolite)<sup>-1</sup>). Moreover, the peak-top temperature of each h-peak was almost the same. These results reveal that the acidic strength and amount of ZSM-5 zeolite within the core-shell particles was unchanged during mechanochemical treatment.

### 3.2. Catalytic performance on ETP reaction

The parent ZSM-5, TiO<sub>2</sub>(mc)/ZSM-5\_800, and TiO<sub>2</sub>(mc)/silicalite-1\_800 were evaluated as catalysts for the ETP reaction at various reaction temperatures. The product yields and

distributions in the ETP reaction are shown in Fig. S8† and listed in Table S1.† As shown in Fig. S8a,† the parent ZSM-5 showed higher C<sub>2</sub>H<sub>4</sub> conversion (85%) at 400 °C, while C<sub>2</sub>H<sub>4</sub> conversion decreased with an increase in the reaction temperature due to the formation of a large amount of coke during the reaction. TiO<sub>2</sub>(mc)/ZSM-5\_800 showed half the conversion (Fig. S8†) of the parent ZSM-5, although the contact time ( $W_{\text{zeolite}}/F_{\text{ethylene}}$ , where  $W$  is the zeolite weight in the catalysts and  $F$  is the flow rate of ethylene) was set to be the same. Possible reasons for the lower conversion are lowering of C<sub>2</sub>H<sub>4</sub> diffusion through the thin TiO<sub>2</sub> layer to ZSM-5 and deactivation of the external acid sites on ZSM-5 due to partial amorphization of the surface of ZSM-5 (ref. 54) or covering by TiO<sub>2</sub> fragments.

TiO<sub>2</sub>(mc)/silicalite-1\_800 showed no C<sub>2</sub>H<sub>4</sub> conversion (Fig. S8c†), because there are no Brønsted acid sites, (≡Al-O(H)-Si≡), in silicalite-1.

### 3.3. OCM reaction over TiO<sub>2</sub>(mc)/ZSM-5 catalyst in an electric field

The TiO<sub>2</sub>/ZSM-5 composite and the related samples were exposed to the CH<sub>4</sub>/O<sub>2</sub> gas flow in an electric field to evaluate the catalytic properties for the OCM reaction. During the reaction, a certain amount of H<sub>2</sub>O was detected. This strongly supports that the OCM reaction successfully occurred in this catalytic system. In addition, the production of H<sub>2</sub> was also observed. It may be caused by the partial oxidation of CH<sub>4</sub> to give H<sub>2</sub> and CO; however, the selectivity to H<sub>2</sub> from CH<sub>4</sub> was still low, which was less than 30%. The OCM reaction is thus pointed out as the main reaction in this catalytic system.

Table 2 summarizes the OCM activities in an electric field over four catalysts: TiO<sub>2</sub>\_800, TiO<sub>2</sub>(pm)/ZSM-5\_800, TiO<sub>2</sub>(mc)/ZSM-5\_800, and TiO<sub>2</sub>(mc)/silicalite-1\_800. The furnace temperature was set at 150 °C; however, during OCM and the over-oxidation reaction to give CO or CO<sub>2</sub>, which are the exothermic reactions, the temperature at the bottom of the catalyst bed was autogenously increased. Although TiO<sub>2</sub>\_800 catalyst made electric field stable during the input current changed from 8.0 to 4.0 mA (Fig. S9a†), the maximum of CH<sub>4</sub> conversion was as low as 1.7%. The selectivity to CO and CO<sub>2</sub> reached *ca.* 94.8% and the yields of

Table 1 Textural properties of samples prepared in this study

Sample	Specific surface area <sup>a</sup> [m <sup>2</sup> (g-bulk) <sup>-1</sup> ]	Micropore volume <sup>b,c</sup> [cm <sup>3</sup> (g-zeolite) <sup>-1</sup> ]
ZSM-5	399	0.17
ZSM-5_800	346	0.14
Silicalite-1	419	0.18
Silicalite-1_800	425	0.18
TiO <sub>2</sub> (pm)/ZSM-5	207	0.16
TiO <sub>2</sub> (pm)/ZSM-5_800	189	0.14
TiO <sub>2</sub> (mc)/ZSM-5	197	0.15
TiO <sub>2</sub> (mc)/ZSM-5_800	182	0.13
TiO <sub>2</sub> (mc)/silicalite-1	197	0.16
TiO <sub>2</sub> (mc)/silicalite-1_800	198	0.16

<sup>a</sup> Specific surface area of catalysts were calculated using the Brunauer-Emmett-Teller (BET) equation based on N<sub>2</sub> adsorption isotherms. Data in the relative pressure range of 3–9 × 10<sup>-3</sup> were employed for the surface area evaluation. <sup>b</sup> Micropore volumes of the catalysts were calculated by the *t*-plot method based on N<sub>2</sub> adsorption isotherms. Data in the relative pressure range of 0.75–0.95 were employed for the *t*-plot analysis. <sup>c</sup> The ideal content of zeolite within the mixtures of TiO<sub>2</sub> and zeolite was 50 wt%.



Table 2 Catalytic activities over various catalysts under application of an electric field

Run	Catalyst	Input current (mA)	Temp. <sup>c</sup> (°C)	Conversion of CH <sub>4</sub> (%)	Selectivity (C%)							Yield (C%)	
					CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> <sup>b</sup>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>
A-1	TiO <sub>2</sub> _800	8.0	307	1.7	86.0	8.8	4.3	0.9	0.0	0.0	0.1	0.02	0.00
A-2		6.0	293	1.5	88.0	6.9	4.4	0.7	0.0	0.0	0.1	0.01	0.00
A-3		4.0	274	0.6	88.4	6.6	5.0	0.9	0.0	0.0	0.0	0.00	0.00
B-1	TiO <sub>2</sub> (pm)/ZSM-5_800	Operation impossible <sup>c</sup>		—	—	—	—	—	—	—	—	—	—
C-1	TiO <sub>2</sub> (mc)/ZSM-5_800	8.0	432	18.4	64.2	3.4	8.5	15.7	6.5	1.7	5.6	2.89	0.32
C-2		6.0	416	11.9	61.5	2.8	12.3	17.4	3.5	2.6	3.9	2.06	0.31
C-3		4.0	350	2.9	64.5	3.2	14.5	8.3	9.5	0.0	0.9	0.24	0.00
D-1	TiO <sub>2</sub> (mc)/silicalite-1_800	8.0	435	8.3	56.2	5.7	10.9	16.4	10.1	0.7	3.1	1.36	0.06
D-2		6.0	418	7.9	55.2	5.8	15.1	17.1	6.0	0.7	3.0	1.35	0.05
D-3		4.0	387	1.1	65.6	4.4	15.9	7.3	3.8	3.1	0.3	0.08	0.03

<sup>a</sup> Catalyst bed temperature measured using a thermocouple. <sup>b</sup> C<sub>2</sub> yield means the sum of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> yields. <sup>c</sup> The intense discharge in the catalyst bed occurred intermittently. The conversion of CH<sub>4</sub>, the selectivity toward products, and the yields of C<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> over (A) TiO<sub>2</sub>\_800, (B) TiO<sub>2</sub>(pm)/ZSM-5\_800, (C) TiO<sub>2</sub>(mc)/ZSM-5\_800, and (D) TiO<sub>2</sub>(mc)/silicalite-1\_800 in the electric field. Reaction conditions: catalyst, 100 mg; preset furnace temperature, 150 °C; feed gas, CH<sub>4</sub> : O<sub>2</sub> : Ar = 25 : 15 : 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>. Pretreatment conditions: furnace temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>.

C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> were very low (<0.1%). TiO<sub>2</sub>(pm)/ZSM-5\_800 caused excessive electric discharge in the catalyst bed, even at an input current of 9.0 mA (Fig. S9b†), because ZSM-5 aluminosilicates are typical insulators with extremely lower electric conductivity; therefore, the catalytic results were not evaluated in this study. TiO<sub>2</sub>(mc)/ZSM-5\_800 and TiO<sub>2</sub>(mc)/silicalite-1\_800 maintained a stable voltage while a current of 9.0 mA was applied (Fig. S9c and d†), which indicates that the thin TiO<sub>2</sub> layer within the core-shell particles enables electrons to conduct between the two electrodes set in the catalyst bed. The TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst exhibited high CH<sub>4</sub> conversion (18.4%) when the input current was 8.0 mA, and a relatively high selectivity toward C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> (8.5 and 15.7%, respectively) with lower selectivity toward CO and CO<sub>2</sub> (64.2 and 3.4%, respectively) was achieved. The CH<sub>4</sub> conversion over TiO<sub>2</sub>(mc)/ZSM-5 (1.5–2.0 μm) was higher than that over TiO<sub>2</sub>(mc)/silicalite-1, which exhibits a low external surface area corresponding to large particle size (ca. 15 μm). It is supposed that the active sites for the O<sub>2</sub> activation and the subsequent CH<sub>4</sub> activation are located on the surface of

TiO<sub>2</sub> nanoparticles, facing to zeolite particles. Therefore, the CH<sub>4</sub> conversion is strongly affected by the external surface area of zeolite particles. Deactivation of the catalyst was not observed during the OCM reaction in electric field. In the TGA of the used catalyst, there was no significant weight loss in the range from 300 to 700 °C due to the deposited coke (Fig. S10†). This indicates that no coke formation occurs during the OCM reaction even in an electric field. In addition, the crystallinities and morphology of the used catalyst were almost remained unchanged (data not shown).

We tried to conduct the <sup>18</sup>O<sub>2</sub> isotope exchange experiment on TiO<sub>2</sub>\_800 and TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst in an electric field (see Fig. S11†). A certain amount of <sup>18</sup>O<sup>16</sup>O molecules was observed over TiO<sub>2</sub>(mc)/ZSM-5\_800, while TiO<sub>2</sub> yielded only traces of <sup>18</sup>O<sup>16</sup>O. We suppose that O<sub>2</sub> close to an oxygen vacancy on the TiO<sub>2</sub> surface can be activated by electrons running through the TiO<sub>2</sub> surface, the active oxygen species subsequently dissociates a H-CH<sub>3</sub> bond to form a methyl radical, yielding C<sub>2</sub> hydrocarbons. This observation is just primitive;

Table 3 Influence of electric field on the catalytic activity of TiO<sub>2</sub>(mc)/ZSM-5\_800

Reaction conditions	Preset furnace temperature (°C)	Input current (mA)	Temp. <sup>c</sup> (°C)	Conversion of CH <sub>4</sub> (%)	Selectivity (C%)							Yield (C%)	
					CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> <sup>b</sup>	C <sub>3</sub> H <sub>6</sub>	
Without EF	450	—	463	0.1	90.3	9.7	0.0	0.0	0.0	0.0	0.0	0.0	0.00
	600	—	612	0.2	93.0	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
	750	—	758	2.4	91.0	7.7	1.1	0.2	0.0	0.0	0.0	0.0	0.00
	900	—	901	16.9	84.9	11.0	1.5	2.5	0.0	0.0	0.7	0.01	
With EF	150	6.0	417	11.3	58.4	2.7	13.6	15.1	7.8	2.5	4.1	0.28	

<sup>a</sup> Catalyst bed temperature measured using a thermocouple. <sup>b</sup> C<sub>2</sub> yield means the sum of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> yields. Reaction conditions: catalyst, 100 mg; feed gas, CH<sub>4</sub> : O<sub>2</sub> : Ar = 25 : 15 : 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>. Pretreatment conditions: furnace temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>.



therefore, the study focusing on the active oxygen species on the TiO<sub>2</sub> surface in an electric field will be reported elsewhere.

### 3.4. Electric field effect on the catalytic activity in the OCM

Table 3 and Fig. S12<sup>†</sup> show the catalytic performance of TiO<sub>2</sub>(mc)/ZSM-5\_800 without application of a voltage but with heating using a furnace at 450, 600, 750, and 900 °C. At 450 °C, no catalytic reactions occurred, whereas at a high temperature of 750 °C, 2.4% of CH<sub>4</sub> conversion was achieved, and a higher reaction temperature gave 16.9%, while high selectivity to CO and CO<sub>2</sub> was unchanged at more than 95%, regardless of the furnace temperature. The maximum C<sub>2</sub> yield (0.7%) with only heating was much lower than that (4.1%) under application of a voltage at a constant current of 6 mA in the catalyst bed. These results indicate that the O<sub>2</sub> activation *via* electrons running through the surface of TiO<sub>2</sub> located at the interface of TiO<sub>2</sub> and zeolite particles under a high voltage, even at lower temperature of 150 °C, induces the OCM reaction without excessive formation of CO and CO<sub>2</sub>, compared to the temperatures higher than 750 °C.

We carefully studied the influence of the input current at the same reaction temperature (*ca.* 450 °C) on the OCM activity over TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst in an electric field (see Table 4). When the preset temperature was fixed at 150 °C (runs 1–3 in Table 4), the catalyst-bed temperature increased as the input current increased. It is due to both exothermic reaction of OCM and joule heating within solid catalyst (detail described in Section 3.6). Hence, by tuning the preset temperature, the catalyst-bed temperature was fixed at *ca.* 450 °C with the different input current (runs 4–6 in Table 4). When the catalyst bed temperature was fixed, the CH<sub>4</sub> conversion linearly increases as the input current increases. This strongly supports that the electrons through the surface of TiO<sub>2</sub> within the composite particles induce the O<sub>2</sub> activation to promote the OCM reaction, regardless of the reaction temperature, at least *ca.* 450 °C. In these reaction conditions, the selectivity to CO and CO<sub>2</sub> was stable at *ca.* 70%, as described above. When the OCM reaction proceeded, C<sub>2</sub>H<sub>6</sub> selectivity decreased while C<sub>2</sub>H<sub>4</sub> selectivity increased; therefore, the possible reaction pathway in this catalytic system will be discussed as described below.

### 3.5. Possible reaction pathway in electric field

The influence of the contact time ( $W/F_{\text{methane}}$ ) on the OCM activity over the TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst under application of a constant current (7.0 mA) and lower reaction temperature (150 °C) was investigated to discuss the possible reaction pathway in this catalytic system. The dependence of OCM activity on the contact time is shown in Fig. 4 and S13,<sup>†</sup> and the overall results are listed in Table S2.<sup>†</sup> The OCM reaction was confirmed to occur as a catalytic reaction over TiO<sub>2</sub>(mc)/ZSM-5\_800 in this reaction system because there is a proportional relation between  $W/F_{\text{methane}}$  and each conversion of CH<sub>4</sub> or O<sub>2</sub>, as shown in Fig. S13.<sup>†</sup> A possible reaction pathway from C1

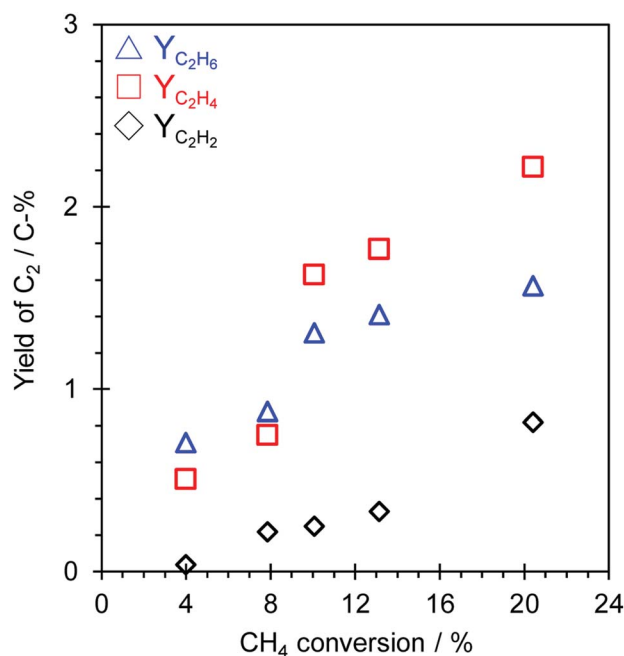


Fig. 4 Relation between CH<sub>4</sub> conversion and C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> yield over TiO<sub>2</sub>(mc)/ZSM-5\_800 under application of an electric field. Reaction conditions: catalyst, 100 mg; input current, 7.0 mA; feed gas, CH<sub>4</sub> : O<sub>2</sub> : Ar = 5x : 3x : 12x (total flow rate: 50, 75, 100, 150, 200 cm<sup>3</sup> (SATP) min<sup>-1</sup>); preset furnace temperature, 150 °C.

Table 4 Influence of different input current on the catalytic activity of TiO<sub>2</sub>(mc)/ZSM-5\_800

Run	Input current	Preset furnace temperature	Temp. <sub>c</sub> <sup>a</sup>	Conversion of CH <sub>4</sub> (%)	Selectivity (C%)						
					CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CO + CO <sub>2</sub>	C <sub>2</sub> yield <sup>b</sup> (C%)
1	3.0	150	370	1.3	54.9	4.4	20.8	9.4	10.6	59	0.5
2	5.0		397	6.8	66.1	3.6	13.3	14.5	2.5	70	2.1
3	7.0		415	10.0	63.3	2.9	13.2	16.3	2.5	66	3.2
4	3.0	374	454	0.9	65.3	5.3	21.2	8.2	0.0	71	0.3
5	5.0	339	449	5.1	71.6	4.2	7.5	8.4	8.3	76	1.2
6	7.0	290	448	10.7	65.2	3.6	11.9	15.6	3.7	69	3.4

<sup>a</sup> Catalyst bed temperature measured using a thermocouple. <sup>b</sup> C<sub>2</sub> yield means the sum of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> yields. The selectivity of products, conversion of methane and the yield of C<sub>2</sub> in OCM reaction over TiO<sub>2</sub>(mc)/ZSM-5\_800 with an electric field. Reaction conditions: catalyst, 100 mg; feed gas, CH<sub>4</sub> : O<sub>2</sub> : Ar = 25 : 15 : 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>. Pretreatment conditions: furnace temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>.





radicals into C<sub>2</sub> hydrocarbons (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>) in this reaction system is much more difficult to speculate. Fig. 4 shows each yield of C<sub>2</sub> hydrocarbons in this catalytic system. C<sub>2</sub>H<sub>2</sub> was a minor C<sub>2</sub> hydrocarbon product with a proportional increase dependent on the CH<sub>4</sub> conversion. In the range of low CH<sub>4</sub> conversion (from 4 to 8%), the yield of C<sub>2</sub>H<sub>6</sub> was relatively higher than that of C<sub>2</sub>H<sub>4</sub>. In contrast, the yield of C<sub>2</sub>H<sub>4</sub> jumped up beyond that of C<sub>2</sub>H<sub>6</sub> at higher CH<sub>4</sub> conversion (from 10 to 20%). Although it seems that the dehydrogenation of C<sub>2</sub>H<sub>6</sub> into C<sub>2</sub>H<sub>4</sub> occurs along with the coupling of C1 radicals into C<sub>2</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>4</sub>, the variation of each C<sub>2</sub> yield is even more complicated to determine the reaction pathway from the results obtained here. To evaluate the mechanism of C<sub>2</sub> hydrocarbon formations during OCM in an electric field, oxidative dehydrogenation of ethane (ODH) over TiO<sub>2</sub>(mc)/ZSM-5 catalyst was conducted in electric field at 150 °C. Reaction results are shown in Table S3.† TiO<sub>2</sub>(mc)/ZSM-5 showed high C<sub>2</sub>H<sub>6</sub> conversion and selectivity of C<sub>2</sub>H<sub>4</sub>. The conversion of C<sub>2</sub>H<sub>6</sub> increased with increasing the input current, but the C<sub>2</sub>H<sub>2</sub> selectivity was still low even at the high C<sub>2</sub>H<sub>6</sub> conversion. These results indicate the oxidative dehydrogenation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> easily proceeded over TiO<sub>2</sub>(mc)/ZSM-5 catalyst in an electric field. The formation of C<sub>2</sub>H<sub>2</sub> may occur in other reaction pathways, such as micro-discharge occurred at the interface between the ZSM-5 core and the TiO<sub>2</sub> shell of the core-shell particles, beside the dehydrogenation of C<sub>2</sub>H<sub>4</sub>. At least, we have confirmed that parent ZSM-5 zeolite does not catalyze the reaction from H<sub>2</sub> and CO into hydrocarbons (see Table S4†) that is well known as Fischer-Tropsch reaction,<sup>65,66</sup> regardless of reaction temperature and H<sub>2</sub> partial pressure.

### 3.6. Influence of O<sub>2</sub> partial pressure on the catalytic activity in an electric field

To confirm that active O<sub>2</sub> species is necessary for dissociation of C–H bond in CH<sub>4</sub>, the influence of the O<sub>2</sub> partial pressure on the OCM activity over the TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst under application of a constant current (8.0 mA) and lower reaction temperature (150 °C) was also investigated. The results of the catalytic activity of TiO<sub>2</sub>(mc)/ZSM-5\_800 are listed in Table 5. No catalytic reaction occurred in the absence of O<sub>2</sub>. In this case, the temperature at the bottom of the catalyst bed increased from 150 to 238 °C by Joule heating. On the other hand, the co-

existence of CH<sub>4</sub> and O<sub>2</sub> in an electric field realizes the OCM reaction over this catalyst. In the low range of O<sub>2</sub> partial pressure (3 and 5 vol%), lower CH<sub>4</sub> conversion (<1%) was obtained, whereas the higher O<sub>2</sub> partial pressure (10 and 15 vol%) gave higher CH<sub>4</sub> conversion. The temperature at the bottom of the catalyst bed further increased with the increase of O<sub>2</sub> partial pressure, due to OCM and the over-oxidation reactions to give CO or CO<sub>2</sub>, which are the exothermic reactions. For instance, when the O<sub>2</sub> partial pressure reached 15%, the temperature at the bottom of the catalyst bed increased to 432 °C. The temperature rise due to exothermic reaction was from 238 to 432 °C, which is in good agreement with thermodynamic estimation from the conversion and selectivity.

### 3.7. Formation of C<sub>3</sub>H<sub>6</sub> over TiO<sub>2</sub>/ZSM-5 catalyst

It should be noted that TiO<sub>2</sub>(mc)/ZSM-5\_800 catalyst produced a meaningful yield of C<sub>3</sub>H<sub>6</sub> when the input current was in the range of 4.0 to 8.0 mA, probably due to the ETP reaction catalyzed by the Brønsted acid sites in ZSM-5 within the core-shell particles. In Table 2, the yield of C<sub>3</sub>H<sub>6</sub> increased from 0 to 0.32% with an increase in the yield of C<sub>2</sub>H<sub>4</sub> from 0.24% to 2.89%. Such the limited C<sub>3</sub>H<sub>6</sub> yield may be due to the subsequent oxidation by O<sub>2</sub> into CO or CO<sub>2</sub>. When the ETP reaction with O<sub>2</sub> over TiO<sub>2</sub>(mc)/ZSM-5 catalyst in an electric field was also performed (Fig. S14†), a relatively large amount of C<sub>3</sub>H<sub>6</sub> as well as butenes and pentenes were detected in the lower input O<sub>2</sub> concentration.

The temperature at the bottom of the catalyst bed during the reaction reached 432 °C (when the input current was 8.0 mA), because the OCM reaction is exothermic. At such temperature, the ZSM-5 zeolite can catalyze the ETP reaction, as mentioned above (see also Fig. S8†). The TiO<sub>2</sub>(mc)/silicalite-1\_800 catalyst only yielded a trace amount of C<sub>3</sub>H<sub>6</sub>, in spite of almost the same CH<sub>4</sub> conversion over TiO<sub>2</sub>(mc)/ZSM-5\_800 at 387–435 °C. These results also support that the production of C<sub>3</sub>H<sub>6</sub> in this reaction system is caused by the catalytic ETP reaction on ZSM-5 at the desirable temperature.

Fig. 5 shows a possible reaction pathway. O<sub>2</sub> could be activated *via* electrons running through the surface of TiO<sub>2</sub> located at the interface of TiO<sub>2</sub> and zeolite particles. Such oxygen species could convert CH<sub>4</sub> into CH<sub>3</sub> radical to generate C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. Moreover, C<sub>3</sub>H<sub>6</sub> was also produced by the ETP reaction catalyzed by Brønsted acid sites in the ZSM-5 zeolite.

Table 5 Influence of O<sub>2</sub> partial pressure on the catalytic activity in OCM over TiO<sub>2</sub>(mc)/ZSM-5\_800 in an electric field

Reactant gas (cm <sup>3</sup> (SATP) min <sup>-1</sup> )				Conversion of CH <sub>4</sub> (%)	Selectivity (C%)					
CH <sub>4</sub>	O <sub>2</sub>	Ar	Temp. <sup>a</sup> (°C)		CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> yield <sup>b</sup> (C%)
25	0	75	238	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	3	72	340	0.6	84.2	3.8	10.0	3.8	0.0	0.1
	5	70	350	1.0	81.4	3.1	10.9	4.6	0.0	0.2
	10	65	405	8.1	60.7	2.5	9.9	12.7	11.8	2.8
	15	60	432	18.4	64.2	3.4	8.5	15.7	6.5	5.6

<sup>a</sup> Catalyst bed temperature measured using a thermocouple. <sup>b</sup> C<sub>2</sub> yield means the sum of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> yields. Reaction conditions: catalyst, 100 mg; total flow rate, 100 cm<sup>3</sup> (SATP) min<sup>-1</sup>; input current, 8.0 mA; preset furnace temperature, 150 °C. Pretreatment conditions: furnace temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm<sup>3</sup> (SATP) min<sup>-1</sup>.





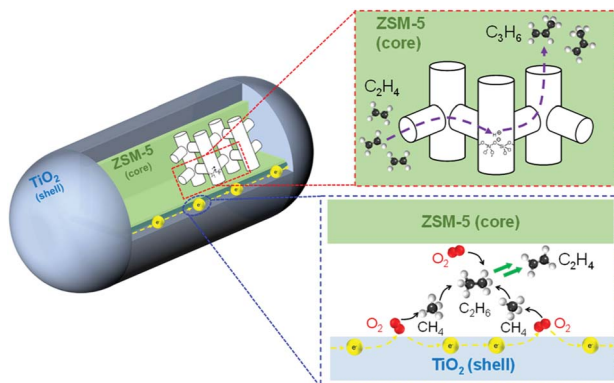


Fig. 5 Illustration of the possible reaction scheme of OCM and ETP reactions over  $\text{TiO}_2(\text{mc})/\text{ZSM-5}$  composite catalyst in an electric field.

### 3.8. Temperature dependence of catalytic activity in an electric field

The catalytic performance of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$  with application of a constant current of 7.0 mA with furnace heating from 150 to 700 °C was evaluated, and the results are shown in Fig. 6 and Table S5.† External heating of the catalyst bed affects the activation of  $\text{CH}_4$ ; the conversion of  $\text{CH}_4$  increased from 13.1 to 22.5% with an increase in the furnace temperature from 150 to

400 °C. In contrast, the  $\text{CH}_4$  conversion decreased significantly to 16.7% when the temperature was increased up to 500 °C and further decreased slightly from 500 to 700 °C. The  $\text{O}_2$  activation and the subsequent  $\text{CH}_4$  conversion may be related to the temperature dependence of the  $\text{TiO}_2$  semiconductivity,<sup>67</sup> in that enhancement of electron conductivity in both  $\text{TiO}_2$  bulk and interface between  $\text{TiO}_2$  nanoparticles may be suppressed by that on the  $\text{TiO}_2$  surface facing to ZSM-5 particles at high temperatures (to be discussed in detail elsewhere). The product selectivity toward  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  with this catalytic system continuously decreased with an increase of the furnace temperature from 150 to 700 °C due to over-oxidation to CO and  $\text{CO}_2$ . Therefore, at higher reaction temperatures, regardless of whether a current is applied in the catalyst bed, only those  $\text{TiO}_2$  nanoparticles that contact each other within the core-shell particles of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}$  may catalyze the complete oxidation of  $\text{CH}_4$  into CO and  $\text{CO}_2$ , which is supported by the high selectivity toward CO and  $\text{CO}_2$  (96.6%) at 900 °C with 23.6% of  $\text{CH}_4$  conversion over the single  $\text{TiO}_2$  catalyst.

## 4. Conclusions

Core-shell ZSM-5 zeolite particles covered with a thin shell layer of  $\text{TiO}_2$  nanoparticles were successfully prepared *via* mechanochemical treatment under high shear stress using a high-performance powder processing machine for application as a unique catalytic system for OCM and subsequent  $\text{C}_3\text{H}_6$  production. A constant current (4.0–8.0 mA) was applied to the catalyst bed of  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$  at a low reaction temperature of 150 °C, which resulted in high methane conversion (18.4%) with selectivity toward  $\text{C}_2\text{H}_6$  (8.5%) and  $\text{C}_2\text{H}_4$  (15.7%), whereas the selectivity toward CO and  $\text{CO}_2$  was relatively low at 64.2% and 3.4%, respectively. In this catalytic system, oxidative coupling of methane at a low temperature under an electric field may be induced by  $\text{O}_2$  activation with electrons moving through the surface of  $\text{TiO}_2$  at the interface between  $\text{TiO}_2$  and zeolite particles under a high voltage. Furthermore, a good amount of  $\text{C}_3\text{H}_6$  was produced during this reaction due to the ETP reaction catalyzed by Brønsted acid sites in ZSM-5 within the core-shell particles. Further improvement of the procedure for preparing a catalyst with a core-shell structure of semiconductive materials and zeolites, and a detailed investigation of the reaction pathways, will be attempted in future work, to progress this energy-sustainable catalytic system with assistance from electron semiconduction at lower reaction temperatures.

## Conflicts of interest

There are no conflicts to declare.

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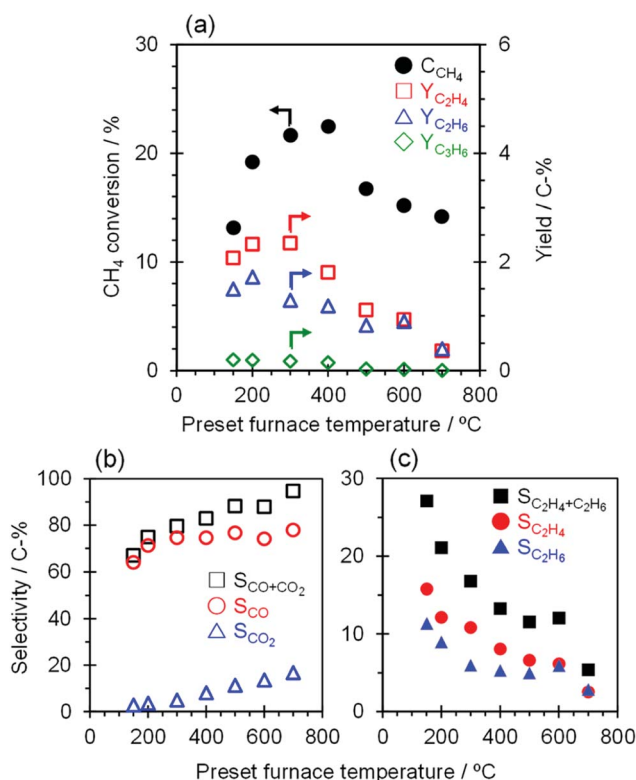


Fig. 6 Temperature dependence over  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$  under application of an electric field. Relation between input furnace temperature and (a)  $\text{CH}_4$  conversion and  $\text{C}_2$  yield, (b) selectivity of CO and  $\text{CO}_2$ , (c) selectivity of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  over  $\text{TiO}_2(\text{mc})/\text{ZSM-5}_{800}$ . Trace amounts of propylene selectivity are not shown in graph (c). Reaction conditions: catalyst, 100 mg; input current, 7.0 mA; feed gas,  $\text{CH}_4 : \text{O}_2 : \text{Ar} = 25 : 15 : 60 \text{ cm}^3 (\text{SATP}) \text{ min}^{-1}$ ; preset furnace temperature, 150–700 °C.



## References

- 1 E. McFarland, *Science*, 2012, **338**, 340–342.
- 2 M. L. Vanessa, A. D. Robert, K. Libor, A. L. Jair, L. K. David and R. P. Daniel, *Catal. Sci. Technol.*, 2012, **2**, 2116–2127.
- 3 P. Tang, Q. J. Zhu, Z. X. Wu and D. Ma, Methane activation: the past and future, *Energy Environ. Sci.*, 2014, **7**(8), 2580–2591.
- 4 T. Peng, Y. X. Wei, M. Ye and Z. M. Liu, *ACS Catal.*, 2015, **5**(3), 1922–1938.
- 5 P. Schwach, X. L. Pan and X. H. Bao, *Chem. Rev.*, 2017, **117**(13), 8497–8520.
- 6 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**(1), 9–19.
- 7 W. Hinsin and M. Baerns, *Chem.-Ztg.*, 1983, **107**(7–8), 223–226.
- 8 T. Ito and J. H. Lunsford, *Nature*, 1985, **314**, 721–722.
- 9 K. Otsuka, K. Jinno and A. Morikawa, *J. Catal.*, 1986, **100**(2), 353–359.
- 10 K. Aika, T. Moriyama, N. Takasaki and E. Iwamatsu, *J. Chem. Soc., Chem. Commun.*, 1986, 1210–1211.
- 11 K. Murata, T. Hayakawa and K. Fujita, *Chem. Commun.*, 1997, 221–222.
- 12 A. Palermo, J. P. Hologado-Vasquez, A. F. Lee, M. S. Tikhov and R. M. Lambert, *J. Catal.*, 1998, **177**(2), 259–266.
- 13 K. Takanabe and E. Iglesia, *Angew. Chem., Int. Ed.*, 2008, **47**(40), 7689–7693.
- 14 U. Zavyalova, M. Holena, R. Schlogl and M. Baerns, *ChemCatChem*, 2011, **3**(12), 1935–1947.
- 15 J. A. Kerr, *Chem. Rev.*, 1966, **66**(5), 465–500.
- 16 C. J. Liu, R. Mallinson and L. Lobban, *J. Catal.*, 1998, **179**(1), 326–334.
- 17 C. J. Liu, R. Mallinson and L. Lobban, *Appl. Catal., A*, 1999, **178**(1), 17–27.
- 18 S. Kado, Y. Sekine and K. Fujimoto, *Chem. Commun.*, 1999, 2485–2486.
- 19 S. Kado, Y. Sekine, T. Nozaki and K. Okazaki, *Catal. Today*, 2004, **89**(1–2), 47–55.
- 20 B. Eliasson, C. J. Liu and U. Kogelshatz, *Ind. Eng. Chem. Res.*, 2000, **39**(5), 1221–1227.
- 21 C. J. Liu, B. Z. Xue, B. Eliasson, F. He, Y. Li and G. H. Xu, *Plasma Chem. Plasma Process.*, 2001, **21**(3), 301–310.
- 22 T. Jiang, Y. Li, C. J. Liu, G. H. Xu, B. Eliasson and B. Z. Xue, *Catal. Today*, 2002, **72**(3–4), 229–235.
- 23 K. Tanaka, Y. Sekine, K. Oshima and Y. Tanaka, *Chem. Lett.*, 2012, **41**(4), 351–353.
- 24 K. Sugiura, S. Ogo, K. Iwasaki, T. Yabe and Y. Sekine, *Sci. Rep.*, 2016, **6**, 25154.
- 25 S. Ogo, K. Iwasaki, K. Sugiura, A. Sato, T. Yabe and Y. Sekine, *Catal. Today*, 2018, **299**, 80–85.
- 26 S. Ogo and Y. Sekine, *Chem. Rec.*, 2017, **17**, 1–14.
- 27 A. Sato, S. Ogo, K. Kamata, Y. Takeno, T. Yabe, T. Yamamoto, S. Matsumura, M. Hara and Y. Sekine, *Chem. Commun.*, 2019, **55**, 4019–4022.
- 28 F. Che, J. T. Gray, S. Ha, N. Kruse, S. L. Scott and J.-S. McEwen, *ACS Catal.*, 2018, **8**(6), 5153–5174.
- 29 G. Pacchioni, *ChemPhysChem*, 2003, **4**, 1041–1047.
- 30 R. Schaub, E. Wahlström, A. Rønnau, E. Lægsgaard, I. Stensgaard and F. Besenbacher, *Science*, 2003, **299**, 377–379.
- 31 X. Y. Pan, M. Q. Yang, X. Z. Fu, N. Zhang and Y. J. Xu, *Nanoscale*, 2013, **5**, 3601–3614.
- 32 M. K. Nowotny, L. R. Sheppard, T. Bak and J. Nowotny, *J. Phys. Chem. C*, 2008, **112**, 5275–5300.
- 33 Y. Y. Yu and X. Q. Gong, *ACS Catal.*, 2015, **5**, 2042–2050.
- 34 S. Lacombe, H. Zanthoff and C. Mirodatos, *J. Catal.*, 1995, **155**, 106–116.
- 35 A. Sato, S. Ogo, Y. Takeno, J. G. Seo and Y. Sekine, *ACS Omega*, 2019, **4**, 10438–10443.
- 36 P. J. Smeets, R. G. Hadt, J. S. Woertink, P. Vanelderren, R. A. Schoonheydt, B. F. Sels and E. I. Solomon, *J. Am. Chem. Soc.*, 2010, **132**(42), 14736–14738.
- 37 P. Vanelderren, J. Vancauwenbergh, B. F. Sels and R. A. Schoonheydt, *Chem. Rev.*, 2013, **257**(2), 483–494.
- 38 V. C. C. Wang, S. Maji, P. P. Y. Chen, H. K. Lee, S. S. Yu and S. I. Chan, *Chem. Rev.*, 2017, **117**(13), 8574–8621.
- 39 E. V. Starokon, M. V. Parfenov, L. V. Pirutko, S. I. Abornev and G. I. Panov, *J. Phys. Chem. C*, 2011, **115**(5), 2155–2161.
- 40 B. E. R. Snyder, P. Vanelderren, M. L. Bols, S. D. Hallaert, L. H. Böttger, L. Ungur, K. Pierloot, R. A. Schoonheydt, B. F. Sels and E. I. Solomon, *Nature*, 2016, **536**, 317–322.
- 41 L. S. Wang, L. X. Tao, M. S. Xie, G. F. Xu, J. S. Huang and Y. D. Xu, *Catal. Lett.*, 1993, **21**(1–2), 35–41.
- 42 Y. Song, Y. B. Xu, Y. Suzuki, H. Nakagome, X. X. Ma and Z. G. Zhang, *J. Catal.*, 2015, **330**, 261–272.
- 43 Y. Song, Q. Zhang, Y. B. Xu, Y. Zhang, K. Matsuoka and Z. G. Zhang, *Appl. Catal., A*, 2017, **530**, 12–20.
- 44 J. Gao, Y. T. Zheng, J. M. Jehng, Y. D. Tang, I. E. Wachs and S. G. Podkolzin, *Science*, 2015, **348**, 686–690.
- 45 B. M. Weckhuysen, D. Wang, M. P. Rosynek and J. H. Lunsford, *J. Catal.*, 1998, **175**(2), 347–351.
- 46 M. Hosokawa, K. Nogi, M. Naito and T. Yokoyama, *Nanoparticle Technology Handbook*, Elsevier, Oxford, U.K., 2007.
- 47 C. Baerlocher, L. B. McCusker and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, Amsterdam, 6th edn, 2007, see also: <http://www.iza-structure.org/databases/>.
- 48 R. J. Argauer and G. R. Landolt, *US Pat.*, US3702886A, November 14, 1972.
- 49 T. F. Narbeshuber, G. Vinek and J. A. Lercher, *J. Catal.*, 1995, **157**(2), 388–395.
- 50 H. Mochizuki, T. Yokoi, H. Imai, R. Watanabe, S. Namba, J. N. Kondo and T. Tatsumi, *Microporous Mesoporous Mater.*, 2011, **145**(1–3), 165–171.
- 51 S. Inagaki, S. Shinoda, Y. Kaneko, K. Takechi, R. Komatsu, Y. Tsuboi, H. Yamazaki, J. N. Kondo and Y. Kubota, *ACS Catal.*, 2013, **3**(1), 74–78.
- 52 B. M. Lin, Q. H. Zhang and Y. Wang, *Ind. Eng. Chem. Res.*, 2009, **48**(24), 10788–10795.
- 53 S. Follmann and S. Ernst, *New J. Chem.*, 2016, **40**, 4414–4419.
- 54 S. Inagaki, K. Sato, S. Hayashi, J. Tatami, Y. Kubota and T. Wakihara, *ACS Appl. Mater. Interfaces*, 2015, **7**(8), 4488–4493.
- 55 M. Niwa and N. Katada, *Catal. Surv. Jpn.*, 1997, **1**, 215–226.



- 56 M. Niwa and N. Katada, *Chem. Rec.*, 2013, **13**, 432–455.
- 57 N. Katada, *Mol. Catal.*, 2018, **458**, 116–126.
- 58 A. W. Czanderna, C. N. R. Rao and J. M. Honig, *Trans. Faraday Soc.*, 1958, **54**, 1069–1073.
- 59 S. R. Yoganarasimhan and C. N. R. Rao, *Trans. Faraday Soc.*, 1962, **58**, 1579–1589.
- 60 K. N. P. Lumar, K. Keizer, A. J. Burggraaf, T. Okubo, H. Nagamoto and S. Morooka, *Nature*, 1992, **358**, 48–51.
- 61 C. Byrne, R. Fagan, S. Hinder, D. E. McCormack and S. C. Pillai, *RSC Adv.*, 2016, **6**, 95232–95238.
- 62 C. Anderson and A. J. Bard, *J. Phys. Chem. B*, 1997, **101**(14), 2611–2616.
- 63 K. Okada, N. Yamamoto, Y. Kameshima and A. Yasumoti, *J. Am. Ceram. Soc.*, 2001, **84**(7), 1591–1596.
- 64 S. C. Pillai, P. Periyat, R. George, D. E. McCormack, M. K. Seery, H. Hayden, J. Colreavy, D. Corr and S. J. Hinder, *J. Phys. Chem. C*, 2007, **111**(4), 1605–1611.
- 65 A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**(5), 1692–1744.
- 66 D. Fraenkel and B. C. Gates, *J. Am. Chem. Soc.*, 1980, **102**(7), 2478–2480.
- 67 D. C. Cronmeyer, *Phys. Rev.*, 1952, **87**(5), 876–886.

