## Propylene Synthesis

## **Transformation of Methane to Propylene: A Two-Step Reaction Route Catalyzed by Modified CeO<sub>2</sub> Nanocrystals and Zeolites**\*\*

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The utilization of methane, which is the main constituent of natural gas, coal-bed gas, shale gas, and the vast gas hydrate resources, for the production of chemicals is one of the most important research targets in catalysis. The current technology for chemical utilization of methane involves high-temperature steam reforming to produce syngas, and the subsequent conversion of syngas to methanol, followed by methanol transformation. However, steam reforming of methane is an energy- and cost-intensive process. The direct transformation of methane to valuable chemicals would be the most desirable route, however, despite many efforts it remains difficult to achieve.<sup>[1]</sup> The development of novel catalytic routes for the transformation of methane is of high significance from both practical and fundamental points of view.

Monohalogenomethanes (CH<sub>3</sub>Cl or CH<sub>3</sub>Br) could be alternative platform molecules for the conversion of CH<sub>4</sub> to chemicals. Olah et al. reported the catalytic monohalogenation of CH<sub>4</sub> by Cl<sub>2</sub> or Br<sub>2</sub> over supported superacids or noble metals, followed by hydrolysis of methyl halides to methanol and dimethyl ether.<sup>[2]</sup> Zhou et al. disclosed the conversion of CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> to alkyl bromides by using Br<sub>2</sub>, and the subsequent conversion to oxygenates through stoichiometric reactions with metal oxides.<sup>[3]</sup> GRT, Inc. developed a technology for the transformation of CH4 to various products, particularly liquid hydrocarbon fuels, through the reaction with Br2 via methyl bromides, and claimed that this is a costeffective route.<sup>[4]</sup> In these processes, the generated HCl, HBr, or metal bromides must be oxidized to Cl<sub>2</sub> or Br<sub>2</sub> to complete the catalytic cycle. HBr was demonstrated to be useful for the oxidative bromination of CH4 in the presence of O2 instead of Br<sub>2</sub> over supported Ru or Rh catalysts,<sup>[5]</sup> but the high cost and limited availability of noble metals may hinder the large-scale application of this system. Zn-MCM-48-supported hydrated dibromo(dioxo)molybdenum(VI), which might generate Br<sub>2</sub> during reaction, catalyzed the oxidation of CH<sub>4</sub> to methanol

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and dimethyl ether, but the long-term stability of this system was not confirmed.<sup>[6]</sup> SiO<sub>2</sub>-supported FePO<sub>4</sub> was stable for the oxidative bromination of CH<sub>4</sub>, which provided CH<sub>3</sub>Br with a selectivity of approximately 50 %.<sup>[7]</sup> Only a few studies have been devoted to the oxidative chlorination of CH<sub>4</sub> to CH<sub>3</sub>Cl, although HCl is cheaper than HBr. Lercher and co-workers found that LaCl<sub>3</sub> was a superior catalyst for this reaction, which provided CH<sub>3</sub>Cl with a selectivity of around 55 % at a CH<sub>4</sub> conversion of 12 % at 748 K.<sup>[8]</sup>

Herein, we present a novel catalytic route for the conversion of CH<sub>4</sub> to propylene via monohalogenomethane. Propylene is one of the most important bulk chemicals, and currently, it is mainly produced as a coproduct of ethylene through the cracking of naphtha. However, the demand for propylene is growing much faster than the demand for ethylene.<sup>[9]</sup> The development of novel routes for the production of propylene, for example, dehydrogenation of propane,<sup>[9]</sup> conversion of methanol to propylene,<sup>[10]</sup> and conversion of ethylene to propylene,<sup>[11]</sup> has attracted much attention. Our two-step route from CH<sub>4</sub> to propylene can be expressed by Equations (1) and (2). Both reactions are exothermic (see the Supporting Information for details). The net reaction is the oxidation of  $CH_4$  by  $O_2$  to propylene and  $H_2O$  [Eq. (3)]. The development of efficient catalysts for the two reaction steps is the key to this new route.

CH <sub>4</sub> + HCl (HBr) + 1/2 O <sub>2</sub>		catalyst A	CH <sub>3</sub> CI (CH <sub>3</sub> Br) + H <sub>2</sub> O	(1)
	CH <sub>3</sub> Cl (CH <sub>3</sub> Br)	catalyst B	1/3 C <sub>3</sub> H <sub>6</sub> + HCl (HBr)	(2)
Net:	CH <sub>4</sub> + 1/2 O <sub>2</sub>		1/3 C <sub>3</sub> H <sub>6</sub> + H <sub>2</sub> O	(3)

We have investigated the catalytic performances of a variety of non-noble metal catalysts for the oxidative chlorination and bromination of CH<sub>4</sub>. Among various metal oxides, CeO<sub>2</sub> is the most efficient catalyst for both reactions (see Tables S1 and S2 in the Supporting Information). CeO<sub>2</sub> was a particularly good catalyst for the oxidative chlorination of CH<sub>4</sub>; a CH<sub>3</sub>Cl selectivity of 66% and a CH<sub>4</sub> conversion of 12% were attained at 753 K. A higher temperature was required to obtain a similar CH<sub>4</sub> conversion by the oxidative bromination of CH<sub>4</sub>; CH<sub>4</sub> conversion and CH<sub>3</sub>Br selectivity were 16% and 74%, respectively, with  $CeO_2$  at 833 K. Besides CH<sub>3</sub>Cl and CH<sub>3</sub>Br, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Br<sub>2</sub> were also formed in both reactions, but their selectivities were lower. CHCl<sub>3</sub> or CHBr<sub>3</sub> and CCl<sub>4</sub> or CBr<sub>4</sub> were not formed. The product distribution for the oxidative chlorination of CH<sub>4</sub> over CeO<sub>2</sub> is very different from that observed for the radical reaction of  $CH_4/Cl_2$ , the main products of which were  $CH_2Cl_2$  and  $CHCl_3$ .<sup>[2]</sup>

Recent studies have shown that the redox and catalytic properties of CeO<sub>2</sub> may be dependent on morphologies.<sup>[12]</sup> Understanding the effect of morphologies or exposed crystal planes of well-defined CeO<sub>2</sub> nanocrystals may provide an opportunity to unravel the nature of active structures, and is helpful for the rational design of more efficient catalysts. We have studied the effect of the morphology of CeO<sub>2</sub> on its catalytic behaviors in the oxidative chlorination and bromination of CH<sub>4</sub>. We synthesized CeO<sub>2</sub> nanocrystals with the same cubic fluorite phase but different morphologies (nanorod, nanocube, and nano-octahedron) by hydrolysis of cerium(III) salts combined with a hydrothermal treatment.<sup>[12b]</sup> Measurements by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) showed the uniform morphology of our synthesized CeO<sub>2</sub> nanocrystals (Supporting Information, Figure S1). The sizes of the nanorods, nanocubes, and nano-octahedra were  $(9 \pm 4) \times (60 -$ 300) nm, 10-80 nm, and 100-200 nm, respectively. Their specific surface areas measured by N2 adsorption at 77 K were 99, 23, and 21 m<sup>2</sup>g<sup>-1</sup>, respectively. High-resolution TEM (HRTEM) images showed that the nanorods exposed the  $\{110\}$  and  $\{100\}$  planes with fractions of 51% and 49%, respectively, while the nanocubes and the nano-octahedra exposed the {100} and {111} planes with nearly 100%, respectively (Supporting Information, Figure S2). For comparison, CeO<sub>2</sub> nanoparticles with a mean diameter of approximately 9 nm and a surface area of  $146 \text{ m}^2 \text{g}^{-1}$  were also synthesized, and HRTEM images showed that the CeO<sub>2</sub> nanoparticles mainly exposed {111} planes (Supporting Information, Figure S3).

We confirmed that the morphologies of the CeO<sub>2</sub> nanocrystals were sustained after the oxidative chlorination and bromination of CH<sub>4</sub>, although their sizes changed, particularly the length of the nanorods and the size of the nanoparticles (Supporting Information, Figure S3C and Figure S4). We have compared the intrinsic rates of  $CH_4$ conversion  $(r(CH_4))$  and product formation  $(r(CH_3Cl))$  or  $r(CH_3Br)$ ), that is, the amounts of converted  $CH_4$  and formed product at controlled CH<sub>4</sub> conversions per surface area per time unit, among the CeO<sub>2</sub> catalysts with different morphologies (see Figure S5 in the Supporting Information for the calculation of intrinsic rates). The CeO<sub>2</sub> nanorods show the highest  $r(CH_4)$  and  $r(CH_3Cl)$  for the oxidative chlorination of CH<sub>4</sub>, followed by nanocubes, nano-octahedra, and nanoparticles (Table 1). For the oxidative bromination of CH<sub>4</sub>, the nanorods and nanocubes possess similar  $r(CH_4)$  and  $r(CH_3Br)$ , which are higher than the nano-octahedra and nanoparticles. These results suggest that in both reactions the  $\{100\}$  and  $\{110\}$  planes of CeO<sub>2</sub> are more active than the  $\{111\}$ plane.

For the selective oxidation of CH<sub>4</sub> to HCHO by O<sub>2</sub> over most heterogeneous catalysts, the HCHO selectivity decreased sharply with increasing CH<sub>4</sub> conversion, thus leading to very limited HCHO yields (<5%).<sup>[lb,ch]</sup> For the oxidative chlorination or bromination of CH<sub>4</sub> over CeO<sub>2</sub> nanocrystals, CH<sub>3</sub>Cl or CH<sub>3</sub>Br selectivities decreased only modestly with increasing CH<sub>4</sub> conversion by increasing the **Table 1:** Rates of methane conversion and product formation over CeO<sub>2</sub> nanocrystals with different morphologies and nanoparticles.<sup>[a]</sup>

Catalyst	Exposed planes	Surface area <sup>[b]</sup> [m <sup>2</sup> g <sup>-1</sup> ]	r(CH <sub>4</sub> ) [mmol m <sup>-2</sup> h <sup>-1</sup> ]	<i>r</i> (CH <sub>3</sub> X) [mmol m <sup>-2</sup> h <sup>-1</sup> ]
A) Oxidative of	chlorination			
Nanorod	{100} + {110}	54	0.93	0.64
Nanocube	{100}	20	0.72	0.54
Nano- octahedron	{111}	19	0.69	0.45
Nanoparticle	{111}	68	0.57	0.38
B) Oxidative b	promination			
Nanorod	{100} + {110}	52	0.63	0.42
Nanocube	{100}	18	0.62	0.47
Nano- octahedron	{111}	10	0.54	0.38
Nanoparticle	{111}	64	0.50	0.32

[a] Reaction conditions: A) T=753 K,  $CH_4/HCl/O_2/N_2/He=4/2/1/1.5/$ 1.5, total flow rate=40 mLmin<sup>-1</sup>; B) T=873 K, 40 wt% HBr aqueous solution 4.0 mLh<sup>-1</sup>,  $CH_4/O_2/N_2=4/1/1$  (flow rate=15 mLmin<sup>-1</sup>). [b] The specific surface areas listed here are those measured for the used catalysts. X=Cl, Br.

amount of catalyst (Figure 1). Moreover,  $CH_3Cl$  or  $CH_3Br$  selectivity depended on the morphology of  $CeO_2$ . The nanocubes, which exposed {100} planes, were the most selective catalysts, while the nano-octahedra and nanoparticles exposing mainly {111} planes were the least selective for the  $CH_3Cl$  or  $CH_3Br$  formation.

We performed in situ Raman spectroscopic studies for  $CeO_2$  catalysts under the reaction conditions. Only Raman bands ascribed to  $CeO_2$  were observed, and no  $CeCl_3$  or



Figure 1. Selectivities of CH<sub>3</sub>Cl (A) and CH<sub>3</sub>Br (B) formations versus CH<sub>4</sub> conversions in the oxidative chlorination and bromination of CH<sub>4</sub> over CeO<sub>2</sub> nanocrystals with different morphologies and the modified CeO<sub>2</sub> nanocrystals. Reaction conditions: A) T = 753 K, CH<sub>4</sub>/HCl/O<sub>2</sub>/N<sub>2</sub>/He = 4/2/1/1.5/1.5, total flow rate = 40 mLmin<sup>-1</sup>; B) T = 873 K, 40 wt% HBr aqueous solution 4.0 mLh<sup>-1</sup>, CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>=4/1/1 (flow rate = 15 mLmin<sup>-1</sup>). ● NiO-CeO<sub>2</sub> cube, ■ FeO<sub>x</sub>-CeO<sub>2</sub> rod,  $\odot$  cube,  $\Box$  rod,  $\triangle$  octahedron,  $\diamond$  particle.

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CeOCl was formed under the reaction conditions (see Figure S6 in the Supporting Information for the results of  $CeO_2$  nanocubes). This suggests that  $CeO_2$  is the active phase. Concerning the nature of the structure sensitivity (different catalytic behaviors of different exposed planes), theoretical studies showed that the  $\{111\}$  plane of CeO<sub>2</sub> has the lowest surface energy, followed by the  $\{110\}$  and  $\{100\}$  planes.<sup>[13]</sup>  $CeO_2$  nanoparticles, which mainly expose {111} planes, show lower CO oxidation activity than CeO<sub>2</sub> nanorods and nanocubes.<sup>[12]</sup> Our H<sub>2</sub>-TPR (temperature-programmed reduction) studies showed that the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> was easiest for the nanorods, followed by the nanocubes, nano-octahedra, and nanoparticles (Supporting Information, Figure S7). This is in agreement with the CH<sub>4</sub> conversion rates for CeO<sub>2</sub> catalysts with different morphologies. We have proposed a possible reaction mechanism for the oxidative chlorination and bromination of CH<sub>4</sub> over CeO<sub>2</sub> catalysts (Supporting Information, Figure S8). We suggest that the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> plays a key role in the activation of HCl or HBr to form an active Cl or Br species for CH<sub>4</sub> conversion, and the reduced  $Ce^{3+}$  is reoxidized to  $Ce^{4+}$  by O<sub>2</sub>.

We have examined the effect of various additives on the catalytic performances of CeO<sub>2</sub> nanocrystals, and found that, compared to single CeO<sub>2</sub> nanorod or nanocube, the 15 wt %  $FeO_r$ -CeO<sub>2</sub> nanorod and the 10 wt% NiO<sub>r</sub>-CeO<sub>2</sub> nanocube provided improved performances, especially selectivities; CH<sub>3</sub>Cl and CH<sub>3</sub>Br selectivities of 74% and 82% were attained at CH<sub>4</sub> conversions of 23% and 22%, respectively (Figure 1). Solid-solution phases were formed between  $FeO_r$ or NiO with CeO<sub>2</sub> in the composites, and the heteroatoms in CeO<sub>2</sub> might promote the adsorption and activation of HCl or HBr to form active Cl or Br species (Supporting Information, Figure S8). The FeO<sub>x</sub>-CeO<sub>2</sub> nanorod and NiO<sub>x</sub>-CeO<sub>2</sub> nanocube catalysts were stable during the oxidative chlorination and bromination of CH<sub>4</sub>. During these reactions, the selectivities of CH<sub>3</sub>Cl and CH<sub>3</sub>Br stayed almost unchanged over approximately 100 hours, and CH<sub>3</sub>Cl and CH<sub>3</sub>Br could be sustained in more than 15% yields over these catalysts (Figure 2).

For the second step, that is, the conversion of CH<sub>3</sub>Cl or CH<sub>3</sub>Br to olefins, only few studies have been reported. A few research groups showed that zeolite SAPO-34 could catalyze the formation of lower olefins from CH<sub>3</sub>Cl and CH<sub>3</sub>Br, but the selectivity of the formation of C<sub>2</sub>H<sub>4</sub> was higher than that of C<sub>3</sub>H<sub>6</sub>, which was on the level of 20–40 %.<sup>[14–16]</sup> SAPO-34 underwent quick deactivation in a few hours in these reactions. Li<sup>+</sup>-exchanged ZSM-5 could catalyze the CH<sub>3</sub>Cl conversion, but the C<sub>3</sub>H<sub>6</sub> selectivity was also low.<sup>[17]</sup> We first compared the catalytic performances of several H-form zeolites for the conversion of CH<sub>3</sub>Br, and found that H-ZSM-5 exhibited a markedly higher CH<sub>3</sub>Br conversion and a moderate C<sub>3</sub>H<sub>6</sub> selectivity (Supporting Information, Table S3).

We have succeeded in improving  $C_3H_6$  selectivity by treating H-ZSM-5 with an aqueous solution of NH<sub>4</sub>F followed by calcination. By increasing the concentration of NH<sub>4</sub>F (expressed as the molar ratio of F/Si) used for H-ZSM-5 treatment,  $C_3H_6$  selectivity increased significantly for both CH<sub>3</sub>Br and CH<sub>3</sub>Cl conversions (Table 2). At the same time,



**Figure 2.** Dependences of catalytic performances on time on stream for the oxidative chlorination of CH<sub>4</sub> over the 15 wt% FeO<sub>x</sub>–CeO<sub>2</sub> nanorods (A) and the oxidative bromination of CH<sub>4</sub> over the 10 wt% NiO–CeO<sub>2</sub> nanocubes (B). Reaction conditions: A) catalyst (0.50 g), T=753 K, CH<sub>4</sub>/HCl/O<sub>2</sub>/N<sub>2</sub>/He=4/2/1/1.5/1.5, total flow rate=40 mLmin<sup>-1</sup>; B) catalyst (1.0 g), T=873 K, 40 wt% HBr aqueous solution 4.0 mLh<sup>-1</sup>, CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>=4/1/1 (flow rate=15 mLmin<sup>-1</sup>).  $\blacksquare$  CH<sub>3</sub>X selectivity,  $\bigcirc$  CH<sub>4</sub> conversion,  $\blacksquare$  CH<sub>3</sub>X yield,  $\triangle$  CO<sub>x</sub> selectivity,  $\blacklozenge$  CH<sub>2</sub>X<sub>2</sub> selectivity. X=Cl (A), X=Br (B).

the selectivities of the formation of  $C_2-C_4$  alkanes and  $C_2H_4$  decreased correspondingly. Besides the products listed in Table 2,  $C_x$  hydrocarbons ( $x \ge 5$ ), particularly aromatic compounds, were also formed and the selectivity of their formation decreased when the F/Si ratio was increased. While an F/Si ratio that was too high was disadvantageous to the conversion of CH<sub>3</sub>Br or CH<sub>3</sub>Cl, the decrease in the activity was insignificant at proper F/Si ratios. The F-modified

**Table 2:** Effect of modification of H-ZSM-5 by  $NH_4F$  for the conversions of  $CH_3Br$  and  $CH_3Cl.^{[a]}$ 

		5						
F/Si	Conv.	Conv. Selectivity <sup>[b]</sup> [%]						
ratio	[%]	$CH_4$	$C_{2-4}^{0[c]}$	$C_2H_4$	C₃H <sub>6</sub>	$C_4H_8$	C₃H <sub>6</sub> [%]	
A) CH <sub>3</sub>	Br conve	rsion						
0	92	1.2	23	13	30	13	28	
0.031	98	0.9	11	11	38	20	38	
0.047	98	1.0	5.0	7.5	46	25	45	
0.063	94	1.4	1.5	4.3	56	23	53	
0.079	87	1.5	0.4	3.1	59	25	51	
0.095	35	3.5	0	1.8	63	30	23	
B) CH <sub>3</sub> Cl conversion								
0	88	1.6	37	18	18	5.8	16	
0.031	83	1.9	26	20	27	9.9	22	
0.047	89	1.0	8.1	12	46	20	41	
0.063	76	1.3	1.1	4.8	64	23	49	
0.079	68	1.4	0.6	3.5	67	23	45	
0.095	55	1.3	0.5	3.0	67	26	37	

[a] Reaction conditions: A) catalyst (0.10 g), T = 673 K, P-(CH<sub>3</sub>Br) = 9.2 kPa, flow rate = 11 mLmin<sup>-1</sup>, time on stream = 2 h; B) catalyst (0.30 g), T = 673 K,  $P(CH_3CI) = 3.3$  kPa, flow rate = 15 mLmin<sup>-1</sup>, time on stream = 2 h. [b] The remaining products were C<sub>x</sub> hydrocarbons (x  $\geq$  5). [c] C<sub>2</sub>-C<sub>4</sub> alkanes. H-ZSM-5 with an F/Si ratio of 0.063 afforded the best  $C_3H_6$ formation activity in both CH<sub>3</sub>Br and CH<sub>3</sub>Cl conversions;  $C_3H_6$  selectivities of 56% and 64% were attained at CH<sub>3</sub>Br and CH<sub>3</sub>Cl conversions of 94% and 76%, respectively. To the best of our knowledge, these superior  $C_3H_6$  formation performances have to date never been achieved in the conversions of halogenomethanes.

The rapid deactivation was a serious problem for zeolitecatalyzed CH<sub>3</sub>Cl and CH<sub>3</sub>Br conversions.<sup>[14-17]</sup> Our results revealed that H-ZSM-5 was also deactivated seriously in CH<sub>3</sub>Cl conversion (Supporting Information, Figure S9). However, the modification by fluorine significantly improved the stability of the catalyst. With the F-modified H-ZSM-5 (F/Si = 0.063), C<sub>3</sub>H<sub>6</sub> selectivity kept almost unchanged, and CH<sub>3</sub>Cl conversion decreased only slightly within 50 hours (Figure 3 A). Moreover, the regeneration of the catalyst was possible by a simple treatment in air at the reaction temperature for two hours. The F-modified H-ZSM-5 was also stable in the conversion of CH<sub>3</sub>Br to C<sub>3</sub>H<sub>6</sub> (Figure 3 B).



**Figure 3.** Catalytic performances of F-modified H-ZSM-5 versus time on stream for the conversions of CH<sub>3</sub>Cl (A) and CH<sub>3</sub>Br (B). Reaction conditions: A) catalyst (0.30 g), T = 673 K,  $P(CH_3Cl) = 3.3$  kPa, flow rate = 15 mLmin<sup>-1</sup>; B) catalyst (0.10 g), T = 673 K,  $P(CH_3Br) = 9.2$  kPa, flow rate = 11 mLmin<sup>-1</sup>.  $\bigcirc$  CH<sub>3</sub>X conversion,  $\square$  C<sub>3</sub>H<sub>6</sub> selectivity,  $\bullet$  C<sub>3</sub>H<sub>6</sub> yield. X = Cl (A), X = Br (B)

We have characterized the F-modified H-ZSM-5 to gain insights into the nature of F modification. Powder X-ray diffraction (XRD) measurements showed that the modification did not significantly change the crystalline structure of ZSM-5 (Supporting Information, Figure S10). However, the acidity and porous structure of ZSM-5 underwent significant changes after modification. The concentration of the acid sites, particularly the strong Brønsted acid sites, was dramatically decreased after F modification (Supporting Information, Figure S11). The same phenomenon was also observed previously and was proposed to contribute to the inhibition of catalyst deactivation in the dehydro-aromatization of CH<sub>4</sub> to benzene.<sup>[18]</sup> The weakened acidity may also be beneficial to catalyst stability in our case. Moreover, the decrease in the strong Brønsted acidity may suppress the hydrogen transfer and the aromatization reactions,<sup>[19]</sup> and thus contribute to the increase in  $C_3H_6$  selectivity by inhibiting the formations of lower alkanes and aromatic compounds (Table 2).

We found that, in addition to the micropores with sizes of 0.51–0.55 nm, which is typical for ZSM-5, new micropores with sizes of 0.73–0.78 nm were generated after F modification (Supporting Information, Figure S12). The generation of the larger micropores was confirmed by the adsorption studies with *p*-xylene and *o*-xylene (Supporting Information, Table S4). This may be due to the F-induced desilication in peculiar positions of ZSM-5.<sup>[20]</sup> We speculate that the interaction of the F<sup>-</sup> anions with the nearby framework Si may produce SiF<sub>4</sub> gas, particularly at the calcination stage, thus creating larger micropores (Supporting Information, Figure S13).

For the formation of lower olefins from both CH<sub>3</sub>OH and CH<sub>3</sub>Cl the "hydrocarbon pool" mechanism has been proposed, in which the lower olefins are believed to be generated via methylbenzene intermediates.<sup>[10b,21]</sup> We have characterized the hydrocarbon intermediates with our catalysts by a method reported previously,<sup>[22]</sup> and observed various methylbenzenes over H-ZSM-5 and F-modified H-ZSM-5 (Supporting Information, Table S5). It is of significance that the distribution of methylbenzenes is different over the two catalysts, and the modification by F increased the fraction of tetra-, penta-, and hexa-benzenes, which are proposed mainly for C<sub>3</sub>H<sub>6</sub> formation.<sup>[22]</sup> The generated larger micropores in the F-modified H-ZSM-5 may account for this change in the distribution of the intermediates in the hydrocarbon pool on catalyst surfaces. Based on these results, we have proposed reaction mechanisms for the conversions of CH<sub>3</sub>Cl or CH<sub>3</sub>Br over H-ZSM-5 and F-modified H-ZSM-5 catalysts (Supporting Information, Figure S14).

In conclusion, we have developed novel and efficient catalysts for a new two-step route for the production of propylene from methane via  $CH_3Cl$  or  $CH_3Br$ .  $CeO_2$  is an efficient and stable catalyst for the oxidative chlorination and bromination of methane to  $CH_3Cl$  and  $CH_3Br$ . The catalytic properties of  $CeO_2$  are dependent on its morphology or the exposed crystalline planes. The modification of  $CeO_2$  nanocrystals by  $FeO_x$  or NiO could enhance the selectivity of  $CH_3Cl$  or  $CH_3Br$  formation. For the second step, an F-modified H-ZSM-5 is highly selective and stable for the conversions of both  $CH_3Cl$  and  $CH_3Br$  into propylene.

It is noteworthy that Periana et al.<sup>[23]</sup> once developed an efficient two-step conversion of methane to methanol via methyl bisulfate by using oleum as an oxidant. However, this system suffers from the difficulties in the separations of product and catalyst from the oleum medium and in the recovery and reoxidation of the produced SO<sub>2</sub>. In contrast, the product can be easily separated from our heterogeneous catalytic system. Although HCl and HBr are not particularly environmentally friendly, the easy separation and recycling of HCl or HBr in our case could avoid their net release. The overall efficiencies for HCl and HBr were estimated to be 65–70% and 90–93%, respectively, without considering the uses of  $CH_2Cl_2$  and  $CH_2Br_2$  formed in the first step (see Supporting Information for details). Future studies are needed to further



improve the selectivity of target products and to elucidate the detailed reaction mechanism for each step.

## **Experimental Section**

CeO<sub>2</sub> nanocrystals with different morphologies as well as CeO<sub>2</sub> nanoparticles with a large surface area were synthesized by hydrolysis of Ce(NO<sub>3</sub>)<sub>3</sub> in alkaline medium, followed by hydrothermal treatment.<sup>[12b]</sup> The morphologies were controlled by varying the alkaline media, Ce(NO<sub>3</sub>)<sub>3</sub> concentrations, and the hydrothermal conditions. The FeO<sub>x</sub>-CeO<sub>2</sub> nanorods and NiO<sub>x</sub>-CeO<sub>2</sub> nanocubes were prepared by adding Fe(NO<sub>3</sub>)<sub>3</sub> and NiCl<sub>2</sub> into aqueous solutions of Ce(NO<sub>3</sub>)<sub>3</sub>, followed by hydrolysis and hydrothermal treatment procedures used for syntheses of CeO2 nanorods and nanocubes, respectively. H-ZSM-5 (Si/Al = 100) was used for CH<sub>3</sub>Cl and CH<sub>3</sub>Br conversions. The Fmodified H-ZSM-5 was prepared by treating the H-ZSM-5 with aqueous solutions of NH4F in different concentrations. After drying at 343 K, the samples were calcined at 873 K for 6 h. XRD, N<sub>2</sub> or Ar physisorption, SEM, TEM, NH<sub>3</sub>-TPD (temperature-programmed desorption), H2-TPR, and in situ Raman spectroscopy were used for catalyst characterizations. Catalytic reactions were performed on fixed-bed flow reactors operated under atmospheric pressure. The products were analyzed by gas chromatography. The conversion and selectivity for each reaction were calculated on a carbon basis. See the Supporting Information for the experimental details.

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- [1] a) D. Wolf, Angew. Chem. 1998, 110, 3545-3547; Angew. Chem. Int. Ed. 1998, 37, 3351-3353; b) K. Tabata, Y. Teng, T. Takemoto, E. Suzuki, M. A. Bañares, M. A. Peña, J. L. G. Fierro, Catal. Rev. 2002, 44, 1-58; c) A. Arena, A. Parmalina, Acc. Chem. Res. 2003, 36, 867-875; d) Y. Xu, X. Bao, L. Lin, J. Catal. 2003, 216, 386-395; e) R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas, F. Schüth, Angew. Chem. 2009, 121, 7042-7045; Angew. Chem. Int. Ed. 2009, 48, 6909-6912; f) B. Frank, J. Zhang, R. Blume, R. Schögl, D. S. Su, Angew. Chem. 2009, 121, 7046-7051; Angew. Chem. Int. Ed. 2009, 48, 6913-6917; g) C. Copéret, Chem. Rev. 2010, 110, 656-680; h) Q. Zhang, W. Deng, Y. Wang, Chem. Commun. 2011, 47, 9275-9292; i) H. Schwarz, Angew. Chem. 2011, 123, 10276-10297; Angew. Chem. Int. Ed. 2011, 50, 10096-10115.
- [2] G. A. Olah, B. Gupta, M. Farina, J. D. Felberg, W. M. Ip, A. Husain, R. Karpeles, K. Lammertsma, A. K. Melhotra, N. J. Trivedi, J. Am. Chem. Soc. 1985, 107, 7097-7105.
- [3] X. P. Zhou, A. Yilmaz, G. A. Yilmaz, I. M. Lorkovic, L. E. Laverman, M. Weiss, J. H. Sherman, E. W. McFarland, G. D. Stucky, P. C. Ford, *Chem. Commun.* 2003, 2294–2295.

- [4] http://www.grt-inc.com/go/technology/grt-technology/.
- [5] a) K. X. Wang, H. F. Xu, W. S. Li, X. P. Zhou, J. Mol. Catal. A 2005, 225, 65–69; b) Z. Liu, L. Huang, W. S. Li, F. Yang, C. T. Au, X. P. Zhou, J. Mol. Catal. A 2007, 273, 14–20.
- [6] F. Li, G. Yuan, Angew. Chem. 2006, 118, 6691–6694; Angew. Chem. Int. Ed. 2006, 45, 6541–6544.
- [7] R. Lin, Y. Ding, L. Gong, W. Dong, J. Wang, T. Zhang, J. Catal. 2010, 272, 65–73.
- [8] a) E. Peringer, S. G. Podkolzin, M. E. Jones, R. Olindo, J. A. Lercher, *Top. Catal.* 2006, *38*, 211–220; b) S. G. Podkolzin, E. E. Stangland, M. E. Jones, E. Peringer, J. A. Lercher, *J. Am. Chem. Soc.* 2007, *129*, 2569–2576; c) E. Peringer, M. Salzinger, M. Hutt, A. L. Lemonidou, J. A. Lercher, *Top. Catal.* 2009, *52*, 1220–1231.
- [9] A. H. Tullo, Chem. Eng. News 2003, 81(50), 15-16.
- [10] a) M. Stöcker, *Microporous Mesoporous Mater.* 1999, 29, 3–48;
   b) J. F. Haw, W. Song, D. M. Marcus, J. B. Nicholas, *Acc. Chem. Res.* 2003, *36*, 317–326.
- [11] a) H. Oikawa, Y. Shibata, K. Inazu, Y. Murai, S. Hyodo, G. Kobayashi, T. Baba, *Appl. Catal. A* 2006, *312*, 181–185; b) M. Iwamoto, Y. Kousugi, *J. Phys. Chem. C* 2007, *111*, 13–15; c) M. Taoufik, E. L. Roux, J. Thivolle-Cazat, J. M. Basset, *Angew. Chem.* 2007, *119*, 7340–7343; *Angew. Chem. Int. Ed.* 2007, *46*, 7202–7205; d) B. Lin, Q. Zhang, Y. Wang, *Ind. Eng. Chem. Res.* 2009, *48*, 10788–10795.
- [12] a) K. Zhou, X. Wang, X. Sun, Q. Peng, Y. Li, J. Catal. 2005, 229, 206–212; b) H. X. Mai, L. D. Sun, Y. W. Zhang, R. Si, W. Feng, H. P. Zhang, H. C. Liu, C. H. Yan, J. Phys. Chem. C 2005, 109, 24380–24385; c) N. Ta, M. Zhang, J. Li, H. Li, Y. Li, W. Shen, Catal. Today 2009, 148, 179–183.
- [13] M. Nolan, S. Grigoleit, D. C. Sayle, S. C. Parker, G. W. Watson, Surf. Sci. 2005, 576, 217–229.
- [14] Y. Wei, D. Zhang, Z. Liu, B. L. Su, J. Catal. 2006, 238, 46-57.
- [15] S. Svelle, S. Aravinthan, M. Bjørgen, K. P. Lillerud, S. Kolboe, I. M. Dahl, U. Olsbye, *J. Catal.* **2006**, *241*, 243–254.
- [16] A. Zhang, S. Sun, Z. J. A. Koman, N. Osterwalder, S. Gadewar, P. Stoimenov, D. J. Auerbach, G. D. Stucky, E. W. McFarland, *Phys. Chem. Chem. Phys.* 2011, 13, 2550–2555.
- [17] D. Jaumain, B. L. Su, J. Mol. Catal. A 2003, 197, 263-273.
- [18] Y. Li, L. Liu, X. Huang, X. Liu, W. Shen, Y. Xu, X. Bao, *Catal. Commun.* 2007, 8, 1567–1572.
- [19] M. A. Sanchez-Castillo, R. J. Madon, J. A. Dumesic, J. Phys. Chem. B 2005, 109, 2164–2175.
- [20] a) E. Aubert, F. Porcher, M. Souhassou, V. Petříček, C. Lecomte, J. Phys. Chem. B 2002, 106, 1110-1117; b) M. P. Attfield, C. R. A. Catlow, A. A. Sokol, Chem. Mater. 2001, 13, 4708-4713.
- [21] Y. Wei, D. Zhang, F. Chang, Q. Xia, B. L. Su, Z. Liu, Chem. Commun. 2009, 5999–6001.
- [22] M. Bjørgen, F. Joensen, K. P. Lillerud, U. Olsbye, S. Svelle, *Catal. Today* 2009, 142, 90–97.
- [23] a) R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffer, P. R. Wentrcek, T. Masuda, *Science* 1993, 259, 340-343; b) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* 1998, 280, 560-564.