

Iron-Based Fischer–Tropsch Synthesis for the Efficient Conversion of Carbon Dioxide into Isoparaffins

Shunshun Geng, Feng Jiang, Yuebing Xu, and Xiaohao Liu*^[a]

Iron-based Fischer-Tropsch (FT) synthesis in combination with hydroisomerization in the presence of zeolites for the synthesis of isoparaffins from CO₂/H₂ was conducted in a fixed-bed reactor. Relative to supported iron catalysts, the precipitated one efficiently converted intermediate CO into hydrocarbons by supplying a high density of FT active sites on the catalyst surface. Removing water by interstage cooling and promoting the CO conversion step in the FT synthesis were effective approaches in achieving a high CO₂ conversion, because of an increase in the driving force to the reaction equilibrium. Particle mixing of 92.6 Fe7.4 K with either 0.5 Pd/ β or HZSM-5 zeolite effectively hydroisomerized the resulting FT hydrocarbons into gasoline-range isoparaffins. Particularly, HZSM-5 displayed a higher isoparaffin selectivity at approximately 70%, which resulted from easier hydrocracking and hydroisomerization of the olefinic FT primary products.

The high energy density and ease of transport of gasoline and other liquid hydrocarbons have made them the mainstay of the world's transportation infrastructure. Although researchers continue to pursue the use of low-carbon gases such as methane and hydrogen as transportation fuels and even though electric cars are proliferating, there is no good alternative to liquid fuels for long-distance trucks and other heavy vehicles, as well as aviation.^[1] Given the limited availability of crude oil and the conversion of coal into synthetic liquid fuel by syngas (a mixture of CO and H₂) followed by Fischer–Tropsch synthesis (FTS),^[2-9] this dependence poses major security and environmental problems.^[10] Arguably, the conversion and utilization of such carbon-rich fossil fuels are the main contributors to the emission of the greenhouse gas CO2, which leads to climate change.^[11] Reducing CO₂ emissions must indeed be an urgent and long-term task for sustainable development in the energy and environmental sectors.^[12, 13] It has been confirmed for many years that the hydrogenation reaction is amongst the most important chemical conversions of highly concentrated CO₂.^[11, 14] However, we point out that, authentically, to realize the recycling of CO₂, hydrogen sources cannot be generated

[a]	S. Geng, Dr. F. Jiang, Dr. Y. Xu, Prof. Dr. X. Liu
	The Key Laboratory of Food Colloids and Biotechnology
	Ministry of Education
	School of Chemical and Material Engineering
	Jiangnan University
	Wuxi 214122, Jiangsu Province (P.R. China)
	E-mail: liuxh@jiangnan.edu.cn
	Supporting Information for this article can be found under http://

dx.doi.org/10.1002/cctc.201600058.

by remaining fossil fuels but from splitting water by electrolysis or other cleavage reactions. $^{\left[15-19\right] }$

The aim to reach CO_2 production of fuels has prompted some researchers to focus on FTS by using CO_2 in place of $CO.^{[20-26]}$ Iron catalysts are no doubt the best choice for CO_2 based FTS, because they also catalyze the reverse water-gas shift (RWGS) reaction to cleave one of the oxygen atoms in CO_2 to make CO [Eq. (1)]. The CO thus generated can then be combined with H₂ to make a combination known as renewable syngas, which can be converted into hydrocarbons by FTS [Eq. (2)]. As the chain propagation mechanism of FTS is to synthesize a wide distribution of normal hydrocarbons unsuitable as gasoline fuel, it is desired that a highly selective synthesis of gasoline-range isoparaffins with high octane numbers could be achieved from CO_2 -based FTS followed by subsequent hydroisomerization with a zeolite catalyst [Eq. (3)].

$$\mathrm{CO}_2 + \mathrm{H}_2 \rightarrow \mathrm{CO} + \mathrm{H}_2 \mathrm{O} \qquad \qquad \Delta \mathrm{H}_{\mathrm{573\,K}} = 38 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \qquad (1)$$

$$CO + 2 H_2 \rightarrow (1/n)(C_n H_{2n})$$
 $\Delta H_{573 \, \text{K}} = -166 \, \text{kJ} \, \text{mol}^{-1}$ (2)

$$C_n H_{2n} \rightarrow \text{isomerized hydrocarbons}$$
 (3)

 $\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad \qquad \Delta \mathrm{H_{573\,K}} = -38 \ \mathrm{kJ \ mol^{-1}} \quad (4)$

In the case of CO-based FTS by iron catalysts, the water-gas shift (WGS) reaction [Eq. (4)] may not be avoided under the reaction conditions, and it is directly responsible for the formation of stable CO₂ with a high level of selectivity, which results in low carbon efficiency of converting CO into premium fuels. Given that CO₂ is relatively unreactive and is formed as one of the final products, it is easier to control the CO conversion of the CO-based FTS according to the necessity of the reaction. The direct synthesis of isoparaffins starting from CO/H₂ has been intensively investigated.^[27-31] However, research on the synthesis of the isoparaffins concentrated in the gasoline fraction by using CO₂ is rare. On the basis of the catalytic mechanism of the hydroisomerization of Fischer-Tropsch (FT) products, the overall performance of CO₂ conversion into isoparaffins mainly relies on how CO2-FTS can be optimized considering the catalytic activity and selectivity of the CO_2 feed gas.

 CO_2 -FTS is significantly different from CO-based FTS. First, the feed of the reaction starts from very stable CO_2 molecules. Moreover, in the reversible RWGS reaction, the return of CO_2 from the CO that is formed is a thermodynamically favorable process, and this limits the CO_2 conversion to a low level. Therefore, on the basis of the points mentioned above for the CO_2 -based synthesis of isoparaffins by iron-based FTS, we focused on understanding how the CO_2 conversion could be enhanced with a high carbon efficiency towards renewable iso-



paraffins. Thus, the formation of CO and CH_4 should be suppressed as much as possible. To realize these targets, we investigated K-promoted supported and unsupported iron catalysts and different reaction conditions, reactor systems, and zeolites for the catalytic conversion of CO₂.

All catalytic tests for the selected iron catalysts were conducted in a single fixed-bed reactor. As listed in Table 1, under the reaction conditions of 400 °C, 1 MPa, and 1120 mL $g_{cat}^{-1}h^{-1}$, iron supported on different supports by K-promotion displayed undesirably high selectivities to CO ranging from 23.2 to 54.5% and selectivities to CH₄ ranging from 22.4 to 41.2% at

Table 1. Results measured over supported and unsupported iron-based catalysts in a fixed-bed reactor with $H_2/CO_2=3$.							
Catalyst ^[a]	CO ₂ conversion [%]	Selec [C mc CO	tivity ol %] CH₄	$C_2^{=}-C_4^{=}$	C ₂ °-C ₄ °	C ₅₊	
$\begin{array}{l} 15\text{Fe5}\text{K/SiO}_2^{[b]} \\ 15\text{Fe5}\text{K/}\gamma\text{-Al}_2\text{O}_3^{[b]} \\ 15\text{Fe5}\text{K/AC}^{[b]} \\ 15\text{Fe5}\text{K/}\beta\text{-SiC}^{[b]} \\ 15\text{Fe5}\text{K/}\beta\text{-SiC}^{[c]} \\ 92.6\text{Fe7.4}\text{K}^{[c]} \end{array}$	16.5 40.7 39.5 35.9 17.4 41.7	83.1 23.2 31.9 54.5 58.8 6.0	6.4 41.2 25.4 22.4 3.3 10.3	0.7 4.7 3.5 9.4 4.6 21.6	0.7 23.4 21.1 3.2 1.9 6.2	9.0 7.4 18.1 10.6 31.4 56.0	
[a] Numbers in the catalysts indicate the loading of elements in wt%. [b] 400 °C, 1 MPa, and 1120 mLg _{cat} ⁻¹ h ⁻¹ . [c] 300 °C, 2.5 MPa, and 560 mLg _{cat} ⁻¹ h ⁻¹ .							

similar conversions of approximately 40% (except for 15Fe5K/SiO₂, which was clearly inactive for CO₂ conversion). However, comparing the selectivity to light olefins, that is, C₂⁼ to C₄⁼, the SiC-supported catalyst seemed to be more favorable in terms of the formation of olefins to give a preferential selectivity of approximately 74.6% for C₂⁼ to C₄⁼ in total C₂-C₄ hydrocarbons. Furthermore, the 15Fe5K/β-SiC catalyst was tested at a milder reaction temperature of 300 °C, and it also afforded a similarly high selectivity to CO and C₂⁼ to C₄⁼ (58.8 and 70.8%, respectively). In contrast, the precipitated iron 92.6Fe7.4K catalyst was more beneficial in obtaining overall high performance, and it showed significantly higher activity (41.7%), very low selectivity to CO (6%) and CH₄ (10.3%), and desired high C₂⁼ to C₄⁼ selectivity (77.7%) for CO₂ conversion under the same reaction conditions.

The results above indicate that the precipitated iron catalyst was better suited for further CO reaction to reduce the CO selectivity. Accordingly, the carbon efficiency for CO₂ conversion into usable fuels was greatly improved along with a substantial decrease in the selectivity to CO from 58.8 to 6%. To elucidate how the CO selectivity was effectively suppressed, Figure 1 shows the TEM images of two typical as-prepared 15 Fe5 K/ β -SiC and 92.6 Fe7.4 K catalysts. It is clear that the 15 Fe5 K/ β -SiC catalyst prepared by impregnation exhibits an average size of (3.4±0.7) nm and a homogeneous dispersion of iron oxide nanoparticles on the SiC support. For the unsupported precipitated 92.6 Fe7.4 K catalyst, the average size of the iron oxide particles was much larger at (32.1±13.7) nm than that for the

CHEMCATCHEM Communications



Figure 1. TEM images of the as-prepared a) supported 15 Fe5 K/ β -SiC and b) precipitated 92.6 Fe7.4 K catalysts.



Scheme 1. Reaction network for isoparaffin synthesis by CO₂-based FTS followed by hydroisomerization of the FT products.

supported catalyst and a small number of particularly large particles approximately 80–100 nm in size were observed.

A reaction mechanism for the hydrogenation of CO₂ to hydrocarbons over an iron catalyst is proposed in Scheme 1. The iron catalyst directly catalyzes CO₂ to form hydrocarbons, which is attributed to its activity for the RWGS reaction. CO₂ hydrogenation has been considered to proceed by a two-step process with the initial conversion of CO₂ into CO by the RWGS followed by chain propagation.^[111] On the basis of the reaction approach, the active sites on the iron catalyst should be divided into two types. One is probably an oxidic iron phase, which appears to be active for the RWGS reaction (pathway 1) by abstraction of an O atom in CO₂ by a H radical to form CO. Another is the well-known iron carbide phase (Fe₅C₂) for the dissociation of CO to carbon–carbon propagation by FTS (pathway 3).^[32, 33]



As illustrated in Scheme 1, the hydrogenation of CO_2 over the iron catalyst produces products or intermediates, including CO, water, and hydrocarbons. CO is the reaction intermediate formed in the first step by the RWGS reaction. It further reacts into hydrocarbons as much as possible rather than leaving the catalytic surface. Thus, the overall efficiency of utilizing CO_2 increases with a lower selectivity to CO. In the case of the precipitated iron catalyst, the CO selectivity is highly reduced (6% in Table 1), which might be ascribed to a larger active iron carbide surface, which increases the chances of CO-FTS. In contrast to the precipitated catalyst, the supported iron catalyst has a low concentration of FT active sites on the support. It is thus easier for the formed CO to escape the catalyst surface before further reaction (see Figure S2, Supporting Information), which results in a high CO selectivity (58.8% in Table 1).

Owing to the thermodynamic and chemical stability of CO₂ molecules, as shown in Table 1, the conversion of CO₂ is always limited to approximately 40%, close to the chemical equilibrium, upon performing the hydrogenation of CO₂ under different reaction conditions in a single fixed-bed reactor. Considering the RWGS as a reversible reaction (pathway 2), the driving force for the RWGS reaction can be increased by consuming the CO intermediate to form a hydrocarbon or by decreasing the steam content in the reactor (pathway 4). Given that it is difficult for the monometallic iron catalyst to enhance the conversion of CO₂, it might be feasible to design a bimetallic catalyst in which the other metal is highly active in converting CO into hydrocarbons and inactive for the WGS reaction (pathway 2).^[34] On the basis of this principle, cobalt metal was introduced into the iron catalyst to investigate the CO₂ hydrogenation reaction. Table 2 shows the catalytic results over both the

Table 2. K-promoted FeCo bifunctional catalysts tested for the hydrogenation of $\text{CO}_2^{[a]}$							
Catalyst	CO ₂ conversion [%]	Sele [C m CO	ctivity nol %] CH₄	$C_2^{=}-C_4^{=}$	C ₂ °-C ₄ °	C ₅₊	
92.6 Fe7.4 K ^[b] 88.3 Fe7.1 K4.6 Co ^[b] 84.0 Fe6.7 K9.3 Co ^[b] 15 Co/SiO ₂ ^[c] 15 Co/SiO ₂ ^[b]	41.7 54.6 57.2 45.6 52.2	6.0 2.0 1.6 0.2 4.2	10.3 18.9 22.4 91.8 92.4	21.6 24.4 23.5 0 0	6.2 7.4 8.7 4.1 1.3	56.0 47.0 43.8 3.6 2.2	
[a] Under the conditions of 2.5 MPa, $H_2/CO_2=3$, and 560 mL $g_{cat}^{-1}h^{-1}$. [b] 300 °C. [c] 240 °C.							

cobalt-containing and monometallic iron catalysts. One can see that the introduction of cobalt is notable in promoting the conversion of CO_2 , which increased with an increase in the loading of cobalt. However, a higher selectivity to CH_4 was obtained, despite the increase in the conversion of CO_2 by adding cobalt metal, and this results from the fact that the hydrogenation capability of cobalt metal is higher than that of the iron catalyst. This was confirmed by using the 15 Co/SiO₂ catalyst, by which CH_4 was mainly produced with greater than 90% selectivity at different temperatures. It has been demonstrated that cobalt as a second metal can effectively promote the conversion of CO₂ by accelerating the reaction rate towards the FTS. To enhance the conversion of CO₂, a higher H₂/CO₂ ratio can also be advantageous not only to shift the RWGS reaction to the right side but also to speed up the irreversible FT reaction step. As shown in Table 3, increasing the H₂/CO₂ ratio from 3 to 6 led to an increase in the conversion of CO₂ from 41.7 to 63.9%. Moreover, a higher H₂ concentration also led to the formation of a greater amount of CH₄, lower selectivity to olefins, and a decrease in the probability of chain growth.

Table 3. Effect of H_2/CO_2 ratio on the performance of the hydrogenation of CO_2 over a precipitated 92.6Fe7.4K catalyst. ^[a]							
Molar ratio H_2/CO_2	CO ₂ conversion [%]	Sele [C m CO	ctivity iol %] CH ₄	$C_2^{=}-C_4^{=}$	$C_2^{o} - C_4^{o}$	C ₅₊	
3.0	41.7	6.0	10.3	21.6	6.2	56.0	
4.5	51.1	4.7	13.9	24.8	8.8	47.7	
6.0	63.9	3.1	16.4	21.9	13.5	45.0	
[a] Under the conditions of 300 $^\circ\text{C},$ 2.5 MPa, and 560 mLg _{cat} $^{-1}\text{h}^{-1}.$							

As described in Scheme 1, a large amount of water was also produced in both the RWGS reaction and FT reaction steps during the hydrogenation of CO₂ to hydrocarbons. The water content was approximately twofold higher than that in the conventional FT synthesis starting from feed gas of H₂/CO. The high concentration of water vapor has an inhibiting effect on the reaction rate for the conversion of CO₂, and this is mainly caused by limiting the chemical equilibrium, as the WGS reaction is a favorable process. The chemical equilibrium is affected to a smaller extent by the reaction temperature, as the temperature can clearly not improve the conversion of CO₂. The RWGS reaction is slightly endothermic, and a higher reaction temperature is not helpful to shift the equilibrium but is required to activate stable CO₂ molecules on the basis of thermodynamic and mechanistic reasons. To drive the conversion of CO_2 by shifting the equilibrium, the most effective approach might be by removing water from the reactor (pathway 4). As demonstrated in Figure 2, a two-stage fixed-bed reactor system in series with interstage cooling to condensate the water and hydrocarbons (see Figure S3) can efficiently improve the conversion of CO₂ from 41.7 to 62.3%. Moreover, in this setup the CH₄ selectivity is lowered from 13.5 to 11.4%, and the C₅₊ selectivity is slightly increased from 56 to 61.7%. Suppressing the formation of CH₄ with a two-stage reactor system results from a secondary reaction of the olefins in which the uncondensed gas products in the rich olefins are introduced into the second reactor. Initiating secondary chain growth by re-adsorption of olefins to decrease the selectivity to light hydrocarbons (see Scheme S1) was confirmed in our previous publications.[35-38]

To this end, we studied how to obtain the optimal catalytic activity and selectivity for the conversion of CO_2 by catalyst design, selecting appropriate reaction conditions, and process





Figure 2. CO₂ conversion and product selectivity on the 92.6 Fe7.4 K catalyst measured in different reactor systems at 300 °C and 2.5 MPa with a molar H_2/CO_2 ratio of 3 (in the case of reactor D: 320 °C, H_2/CO_2 =4.5). a) single reactor, 3 g catalyst; b) single reactor, 6 g catalyst; c) two-stage reactor with interstage cooling, 3 g catalyst in each reactor; d) two-stage reactor with interstage cooling, 3 g catalyst in each reactor.

design, which is a basis for developing a highly efficient process of the conversion of CO₂ into isoparaffins by CO₂-FTS. Moreover, the normal hydrocarbon hydroisomerization reaction is also vital for maximum and tailor-made selectivity to isoparaffins in a requisite carbon number range. According to our previous research and as reported in the literature, two kinds of zeolite catalysts have been applied for the hydroisomerization of FT products into isoparaffins.^[31,39] As shown in Table 4, the precipitated 92.6Fe7.4K catalyst for the hydroge-

Table 4. Synthesis of isoparaffins from CO ₂ -FTS with a precipitated 92.6 Fe7.4 K catalyst by combining the hydrocracking of the hydrocarbons by using 0.5 Pd/ β or HZSM-5. ^[a]							
Catalyst	CO ₂ conversion [%]	Select [C mo CO	ivity I%] CH ₄	C _{2~3}	lso-C _{4~6} ^[b] [%]		
$\begin{array}{l} 92.6Fe7.4K\\ 92.6Fe7.4K+0.5Pd/\beta^{[c]}\\ 92.6Fe7.4K+HZSM-5^{[c]}\\ 92.6Fe7.4K+0.5Pd/\beta^{[d]}\\ 92.6Fe7.4K+HZSM-5^{[d]}\\ \end{array}$	41.7 42.7 43.9 32.6 35.1	6.0 6.0 6.1 11.0 22.2	10.3 9.8 9.5 21.7 10.7	19.3 24.5 10.8 31.4 30.1	9.6 51.3 69.7 10.6 28.7		
[a] Under the conditions of 300 $^{\circ}$ C, 2.5 MPa, and 560 mLg _{cat} ⁻¹ h ⁻¹ . [b] Numbers indicate selectivity to isohydrocarbons in total C ₄₋₆ hydrocarbons. [c] Particle mixing. [d] Powder mixing.							

nation of CO₂ produced negligible selectivity to isoparaffins (9.6% in iso-C₄₋₆). Relative to the iron catalyst only, both the 0.5 Pd/ β and HZSM-5 catalysts introduced by particle mixing did not markedly improve the conversion of CO₂ or the selectivities to CO and CH₄. However, the selectivities to C₂₋₃ and iso-C₄₋₆ differed significantly over HZSM-5. As a result, the selectivity to C₂₋₃ remarkably decreased from 19.3 to 10.8% and a very high selectivity to isoparaffin was obtained (69.7% in iso-C₄₋₆). In contrast to HZSM-5, the 0.5Pd/ β catalyst led to a higher C₂₋₃ selectivity from 19.3 to 24.5% and lower isoparaffin selectivity (51.3% in iso-C₄₋₆), which is presumably attribut-

ed to the promotion effect of the hydrogenation of $C_2^{=}-C_3^{=}$ and longer-chain olefins into n-paraffins by hydrogen spillover resulting from the fact that Pd inhibits further chain growth and/or isomerization (see Scheme S2a). In the case of HZSM-5, the higher selectivity to olefins is in favor of hydroisomerization because of a lower activation energy required to form carbonium ions. Also, light olefins such as $C_2^{=}$ and $C_3^{=}$ can add to the carbonium ions to increase the amount of isomers, and this results in a marked decrease in the $C_{2\sim3}$ selectivity (see Scheme S2b). Interestingly, powder mixing of the 92.6Fe7.4K and zeolite catalysts not only lowered the conversion of CO₂ but also produced a small amount of isoparaffins. The acidic sites in the zeolite were poisoned by the K alkali metal in the 92.6 Fe7.4 K catalyst owing to their intimate contact, and this is directly responsible for the decrease in the hydroisomerization activity. At the same time, the 92.6 Fe7.4 K catalyst was also deactivated by the acidic sites in the zeolite, which resulted in a lower conversion of CO₂ and a higher selectivity to CO.

In conclusion, we studied the hydrogenation of CO₂ to liquid fuels (isoparaffins) in a fixed-bed reactor by combining ironbased CO₂ Fischer–Tropsch synthesis (FTS) with subsequent hydroisomerization. Owing to the chemical stability of CO₂ molecules and a limit to the thermodynamic equilibrium, the challenge was to break the equilibrium to obtain a high conversion of CO₂ and a high carbon efficiency to liquid fuels. On the basis of the understanding of the chemical reaction network and the rate-determining step of the CO₂-FTS, we considered that removing water from the reactor and enhancing the conversion rate of CO by the Fischer-Tropsch (FT) reaction were the two most effective approaches to realize the target above. Therefrom, a high conversion of CO₂ with low selectivities to CO and CH4 and olefinic hydrocarbon products were achieved over a precipitated K-promoted iron catalyst in a fixed-bed reactor system in series with interstage cooling to remove water. An improvement in the conversion of CO₂ by removing water was attributed to a decrease in the rate of the water-gas shift reaction. Relative to the impregnated iron catalysts, the precipitated iron catalyst lowered the CO selectivity remarkably by supplying a high density of FT active sites on the catalyst surface, which increased its conversion before it could diffuse out of the catalyst surface. Although adding cobalt metal and increasing the H_2/CO_2 ratio evidently raised the conversion of CO_{2} , the selectivity to CH_4 also increased owing to an increase in the rate of the hydrogenation reaction. For isomerization, HZSM-5 was more favorable in terms of producing isoparaffins by virtue of a mechanism involving the dimerization of highly olefinic FT primary products into higher isomers by carbonium ions. This study provides an efficient approach for the conversion of CO_2 into renewable energy. In the future, CO_2 recycling for the production of chemicals and energy by CO as a reactive intermediate and subsequent chemical conversion by catalysis is bound to attract increasing attention to enable a sustainable society. A key challenge of this strategy for CO₂ utilization is how the selectivity of the products can be controlled under reaction conditions that are difficult to adjust, including the partial pressures of CO and H₂ and their concentrations on the catalyst surface.



Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21576119) and the Natural Science Foundation of Jiangsu Province (BK20151125).

Keywords: carbon dioxide • heterogeneous catalysis • iron • isoparaffins • zeolites

- [1] http://www.sciencemag.org/news/2015/09/feature-there-s-too-muchcarbon-dioxide-air-why-not-turn-it-back-fuel.
- J. C. Kim, S. Lee, K. Na, C. Lee, R. Ryoo, ACS Catal. 2014, 4, 3919–3927.
 Y. Liu, J. Luo, M. Girleanu, O. Ersen, C. Pham-Huu, C. Meny, J. Catal.
- 2014, 318, 179–192.
 [4] X. Peng, K. Cheng, J. Kang, B. Gu, X. Yu, Q. Zhang, Y. Wang, Angew. Chem. 2015, 127, 4636–4639; Angew. Chem. Int. Ed. 2015, 54, 4553–
- 4556.
 [5] K. Keyvanloo, M. K. Mardkhe, T. M. Alam, C. H. Bartholomew, B. F. Woodfield, W. C. Hecker, ACS Catal. 2014, 4, 1071 1077.
- [6] H. Park, D. H. Youn, J. Y. Kim, Y. H. Choi, Y. H. Lee, *ChemCatChem* 2015, 7, 3488 3494.
- [7] J. L. Tu, M. Y. Ding, Q. Zhang, Y. L. Zhang, C. G. Wang, T. J. Wang, L. L. Ma, X. L. Li, *ChemCatChem* **2015**, *7*, 2323–2327.
- [8] H. F. Xiong, L. L. Jewell, N. J. Coville, ACS Catal. 2015, 5, 2640-2658.
- [9] M. Claeys, M. E. Dry, E. van Steen, P. J. van Berge, S. Booyens, R. Crous, P. van Helden, J. Labuschagne, D. J. Moodley, A. M. Saib, ACS Catal. 2015, 5, 841–852.
- [10] T. Morgan, World Energy Outlook 2010, IEC, 2010.
- [11] S. Saeidi, N. A. S. Amin, M. R. Rahimpour, J. CO2 Util. 2014, 5, 66–81.
- [12] C. S. Song, Catal. Today 2006, 115, 2-32.
- [13] G. Centi, E. A. Quadrelli, S. Perathoner, Energy Environ. Sci. 2013, 6, 1711–1731.
- [14] W. Wang, S. P. Wang, X. B. Ma, J. L. Gong, Chem. Soc. Rev. 2011, 40, 3703–3727.
- [15] J. Zhao, T. Minegishi, L. Zhang, M. Zhong, Gunawan, M. Nakabayashi, G. J. Ma, T. Hisatomi, M. Katayama, S. Ikeda, N. Shibata, T. Yamada, K. Domen, *Angew. Chem. Int. Ed.* **2014**, *53*, 11808–11812; *Angew. Chem.* **2014**, *126*, 12002–12006.
- [16] D. Recatalá, R. Llusar, A. L. Gushchin, E. A. Kozlova, Y. A. Laricheva, P. A. Abramov, M. N. Sokolov, R. Gómez, T. Lana-Villarreal, *ChemSusChem* 2015, *8*, 148–157.
- [17] A. J. Clough, J. W. Yoo, M. H. Mecklenburg, S. C. Marinescu, J. Am. Chem. Soc. 2015, 137, 118–121.

- [18] Y. H. Li, P. F. Liu, L. F. Pan, H. F. Wang, Z. Z. Yang, L. R. Zheng, P. Hu, H. J. Zhao, L. Gu, H. G. Yang, *Nat. Commun.* **2015**, *6*, 6916.
- [19] G. L. Zhu, H. Yin, C. Y. Yang, H. L. Cui, Z. Wang, J. J. Xu, T. Q. Lin, F. Q. Huang, *ChemCatChem* **2015**, *7*, 2614–2619.
- [20] D. Mattia, M. D. Jones, J. P. O'Byrne, O. G. Griffiths, R. E. Owen, E. Sackville, M. McManus, P. Plucinski, *ChemSusChem* 2015, *8*, 4064–4072.
- [21] M. K. Gnanamani, G. Jacobs, R. A. Keogh, W. D. Shafer, D. E. Sparks, S. D. Hopps, G. A. Thomas, B. H. Davis, *Appl. Catal. A* **2015**, *499*, 39–46.
- [22] L. M. Chew, P. Kangvansura, H. Ruland, H. J. Schulte, C. Somsen, W. Xia, G. Eggeler, A. Worayingyong, M. Muhler, *Appl. Catal. A* 2014, 482, 163– 170.
- [23] M. Al-Dossary, A. A. Ismail, J. L. G. Fierro, H. Bouzid, S. A. Al-Sayari, Appl. Catal. B 2015, 165, 651–660.
- [24] J. A. Díaz, A. R. de La Osa, P. Sánchez, A. Romero, J. L. Valverde, Catal. Commun. 2014, 44, 57–61.
- [25] U. Rodemerck, M. Holeňa, E. Wagner, Q. Smejkal, A. Barkschat, M. Baerns, ChemCatChem 2013, 5, 1948–1955.
- [26] S. Perathoner, G. Centi, ChemSusChem 2014, 7, 1274-1282.
- [27] Q. H. Lin, G. H. Yang, Q. J. Chen, R. G. Fan, Y. Yoneyama, H. L. Wan, N. Tsubaki, *ChemCatChem* 2015, *7*, 682–689.
- [28] J. Sun, X. G. Li, A. Taguchi, T. Abe, W. Q. Niu, P. Lu, Y. Yoneyarna, N. Tsubaki, ACS Catal. 2014, 4, 1–8.
- [29] J. Bao, J. He, Y. Zhang, Y. Yoneyama, N. Tsubaki, Angew. Chem. Int. Ed. 2008, 47, 353–356; Angew. Chem. 2008, 120, 359–362.
- [30] K. Cheng, L. Zhang, J. C. Kang, X. B. Peng, Q. H. Zhang, Y. Wang, Chem. Eur. J. 2015, 21, 1928–1937.
- [31] B. Sun, G. B. Yu, J. Lin, K. Xu, Y. Pei, S. R. Yan, M. H. Qiao, K. N. Fan, X. X. Zhang, B. N. Zong, *Catal. Sci. Technol.* **2012**, *2*, 1625–1629.
- [32] V. R. R. Pendyala, U. M. Greham, G. Jacobs, H. H. Hamdeh, B. H. Davis, *ChemCatChem* **2014**, *6*, 1952–1960.
- [33] M. K. Gnanamani, H. H. Hamdeh, W. D. Shafer, D. E. Sparks, B. H. Davis, *Catal. Lett.* **2013**, *143*, 1123 – 1131.
- [34] L. G. Yu, X. H. Liu, Y. Y. Fang, C. L. Wang, Y. H. Sun, Fuel 2013, 112, 483– 488.
- [35] X. H. Liu, A. Hamasaki, T. Honma, M. Tokunaga, *Catal. Today* **2011**, *175*, 494–503.
- [36] X. H. Liu, X. H. Li, Y. Suehiro, K. Fujimoto, Appl. Catal. A 2007, 333, 211– 218.
- [37] X. H. Liu, M. Tokunaga, ChemCatChem 2010, 2, 1569–1572.
- [38] N. Tsubaki, K. Yoshii, K. Fujimoto, J. Catal. 2002, 207, 371-375.
- [39] X. H. Li, X. H. Liu, Z. W. Liu, K. Asami, K. Fujimoto, Catal. Today 2005, 106, 154–160.

Received: January 18, 2016 Published online on March 8, 2016