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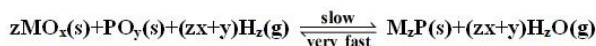
Novel synthesis of NiMoP phosphide catalyst in a CH₄-CO₂ gas mixture

Zhichao Li,^a Qingyou Liu,^{*b} Yan Shi,^a Zhiwei Yao,^{*a} Wei Ding^a and Yue Sun^a

NiMo bimetallic phosphide was synthesized from corresponding oxidic precursor in a 1:1 CH₄:CO₂ gas mixture for the first time. The in-situ synthesized NiMoP phase in the feed for CH₄-CO₂ reforming can exhibit higher activity than the one prepared in H₂.

Transition metal phosphides are a new class of interstitial compounds receiving much attention in recent years due to their widespread applications in various fields, such as electronics, photonics, magnetism, catalysis and so on.¹⁻⁴ In particular, monometallic (e.g. MoP and Ni₂P) and bimetallic (e.g. NiMoP and CoMoP) phosphides have been identified as potential catalysts for many reactions such as hydrogenation and hydrotreating,^{5,6} dry (CO₂) reforming of methane (DRM),^{7,8} N₂H₄ decomposition^{9,10} NO dissociation¹¹ and electrocatalytic reactions including hydrogen evolution, oxygen reduction and evolution reactions.¹²⁻¹⁴

Generally, phosphide catalysts are typically prepared by temperature programmed reduction (TPR) method, in which the reported reducing agents include H₂,⁵ methane¹⁵ and dimethyl ether.¹⁶ Since the formation of phosphide from their corresponding oxidic precursors by H₂-TPR (Scheme 1)^{17,18-24} is thermodynamically unfavorable, the forward reaction has to be aided by high temperature and low water vapor pressure. Thus, phosphides can only be obtained at a low heating rate (e.g. 1 °C min⁻¹) and a high H₂ flow speed (e.g. 300 ml min⁻¹)⁵ to purge the water off the solid surface. In addition, a high concentration of water produced during the reaction process can lead to serious hydrothermal sintering of phosphide particles.^{25,26} In the case of the synthesis using methane and dimethyl ether as reducing agents, the resultant phosphide surface is usually contaminated by carbon deposition from the pyrolysis of CH₄, which can block in the pores and cover the active sites.^{15,16} In this work, we developed a novel synthesis of NiMo bimetallic phosphide catalyst in a 1:1 CH₄:CO₂ gas mixture. Compared with the TPR method using H₂, methane and dimethyl ether as reducing agents, the reaction products included a large amount of CO and H₂ besides H₂O in this novel synthesis route, which can mitigate hydrothermal sintering of phosphide particles and avoid carbon deposition on the surface. Moreover, the in-situ synthesized NiMoP catalyst in the feed for DRM could exhibit higher activity than the one prepared in H₂.



Scheme 1 A simplified equation for the preparation of phosphides by H₂-TPR method.

Fig. 1 shows the XRD patterns of the products from Ni_xMo_yP₁ oxidic precursors with different Ni:Mo molar ratios in CH₄/CO₂ gas mixture. In the case of treating Ni_xMo₁P₁ (x=0, 0.3, 0.6, 1) precursors, the XRD pattern of the product from Ni₀Mo₁P₁ showed the peaks of MoOPO₄ (main peaks at

2θ=25.2, 28.9, 38.7 and 41.3°, PDF 73-2333), indicating that Mo phosphide cannot be in-situ synthesized during DRM. When the Ni (x=0.3) was added into the precursor, the product was composed of MoOPO₄, MoO₂ (main peaks at 2θ=26.0, 36.9, 37.0 and 53.4°, PDF 78-1071) and Ni₂P₂O₇ (main peaks at 2θ=29.6 and 30.6°, PDF 49-1082). With the increase of Ni content from x=0.3 to x=0.6, the MoOPO₄ reflections disappeared, and some weak peaks due to MoP (2θ=32.0 and 43.0°, PDF 65-6487) and NiMoP (main peaks at 2θ=39.2, 43.2 and 47.3°, PDF 31-0873) were detected. With a further increase of Ni content to x=1, the phase composition of the product was predominant NiMoP with very minor Ni₁₂P₅ (main peaks at 2θ=38.4, 41.8, 47.0 and 48.9°, PDF 74-1381) and Mo₃P (main peaks at 2θ=38.0, 42.4, 45.8 and 47.3°, PDF 89-2587). As for Ni₁Mo_yP₁ (y=0, 0.3, 0.6, 1) precursors, they all were reduced to phosphide phases. Note that there was a clear main phase transformation (NiMoP→Ni_xMo_yP²⁷→Ni_xP) with decreasing Mo content from y=1 to y=0 in the oxidic precursors. The results indicated that the increase of Ni/Mo molar ratio in the oxidic precursors can promote the formation of phosphide phase and well crystalline NiMoP phase can be obtained with a stoichiometric ratio of 1:1:1 Ni:Mo:P. The XRD result was in good agreement with the result of H₂-TPR (Fig. 2) that the Ni₁Mo₀P₁ was more easily reduced than Ni₀Mo₁P₁ and the addition of Ni to precursor can facilitate precursor reduction.

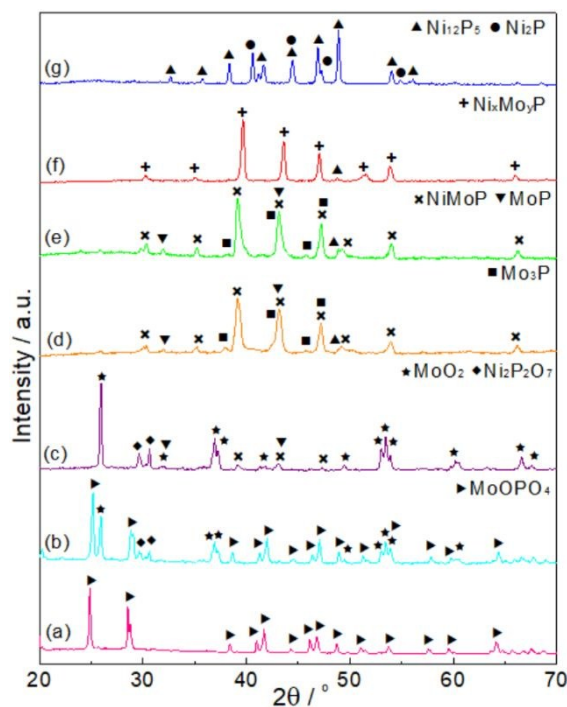


Fig. 1 XRD patterns of materials generated from the Ni_xMo_yP₁ oxidic precursors with different Ni:Mo molar ratios in CH₄/CO₂ gas mixture at 900 °C for 5 h. (a) x=0, y=1, (b) x=0.3, y=1, (c) x=0.6, y=1, (d) x=1, y=1, (e) x=1, y=0.6, (f) x=1, y=0.3 and (g) x=1, y=0.

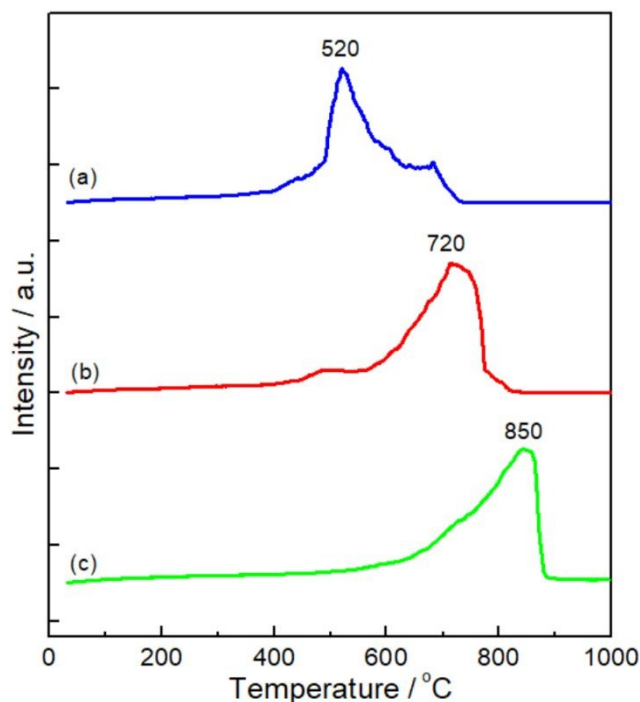


Fig. 2 Profiles of H₂-TPR of (a) Ni₁Mo₀P₁, (b) Ni₁Mo₁P₁ and (c) Ni₀Mo₁P₁ precursors.

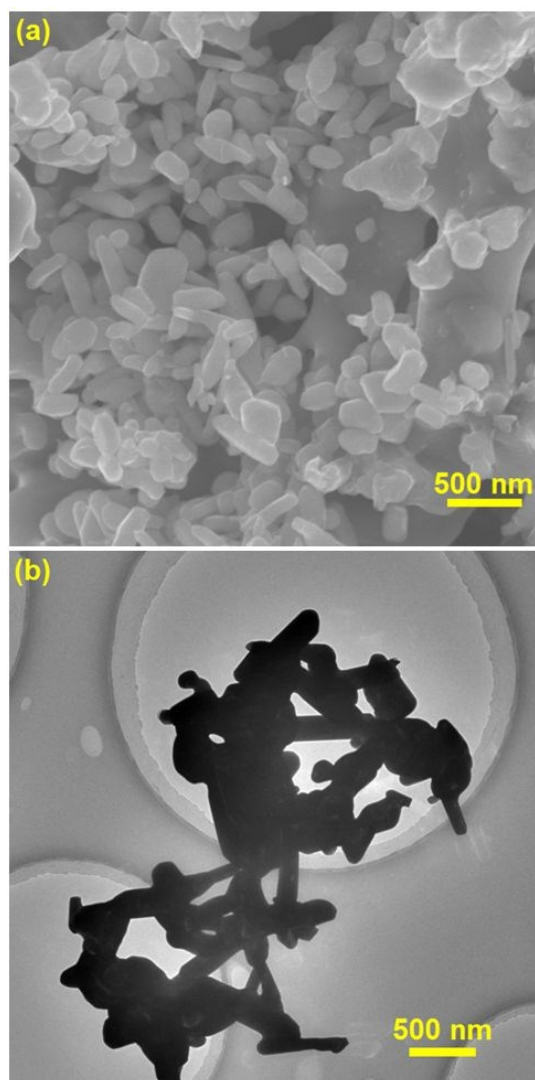


Fig. 4 SEM (a) and TEM (b) images of NiMoP sample prepared from Ni₁Mo₁P₁ oxidic precursor in CH₄/CO₂ gas mixture.

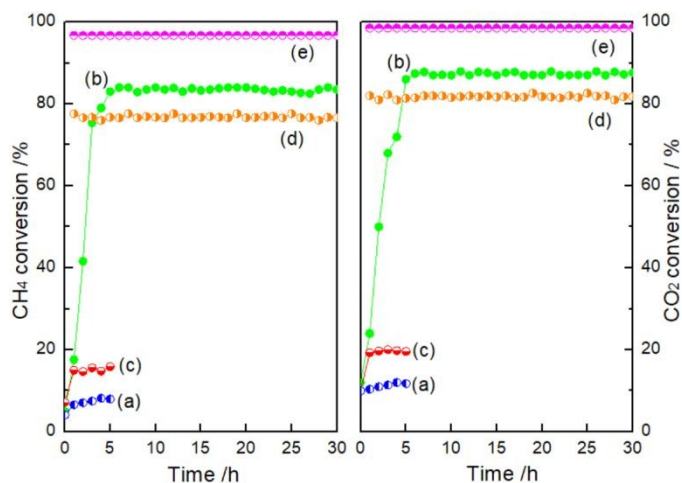


Fig. 5 Catalytic activity of the (a) Ni₀Mo₁P₁, (b) Ni₁Mo₁P₁, (c) Ni₁Mo₀P₁ precursors, (d) H₂-NiMoP in DRM and (e) estimated values of conversions at the reaction equilibrium. Reaction conditions: CH₄:CO₂=1:1, WHSV=9000 cm³ g⁻¹ h⁻¹, reaction pressure= 1 atm, reaction temperature=900 °C.

Whereafter, XPS analysis was used to further determine the surface composition of as-prepared NiMoP sample from Ni₁Mo₁P₁. Fig. 3 shows the XPS spectra of Ni 2p, Mo 3d and P 2p levels for the NiMoP sample. It can be seen that the surface region of the sample was composed of oxidized species and phosphorized species. The binding energies of oxidized Ni (856.0 eV), Mo (228.8 and 232.5 eV) and P (133.1 eV) were agreed with assignments by others to Ni²⁺, Mo⁴⁺/Mo⁶⁺ and P⁵⁺ species,^{28,29} respectively. The binding energies of the peaks at 853.3, 227.9 and 129.8 eV were attributed to Ni^{α+}, Mo^{δ+} and P^{σ-} in phosphide,^{23,26} respectively. The detection of these oxidized species should be attributed to surface oxidation of phosphide in the passivation process.²⁹

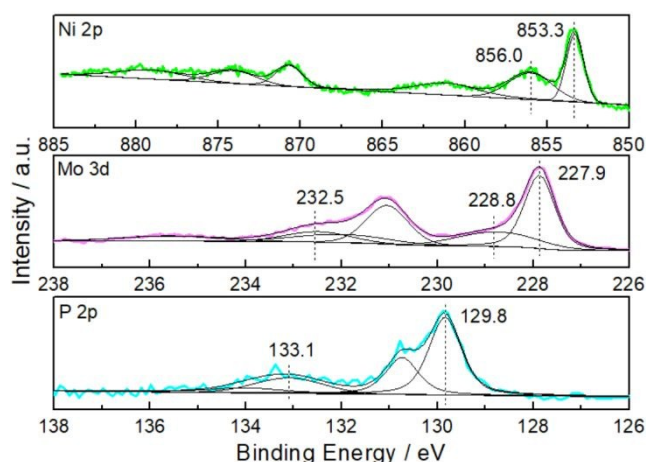


Fig. 3 XPS spectra of Ni 2p, Mo 3d and P 2p regions of NiMoP sample prepared from Ni₁Mo₁P₁ oxidic precursor.

Additionally, the morphology of as-prepared NiMoP sample (hereafter denoted as CH₄/CO₂-NiMoP) from Ni₁Mo₁P₁ was characterized by SEM and TEM. As shown in SEM image (Fig. 4a), the product consisted of aggregates of irregularly rod-shaped particles. The SEM result was in good agreement with the observation of TEM image (Fig. 4b). However, the NiMoP sample (hereafter denoted as H₂-NiMoP) obtained by H₂-TPR consisted of large aggregates of particles (Fig. S1), indicating that serious hydrothermal sintering occurred in this synthesis process.³⁰ Therefore, the surface area of CH₄/CO₂-NiMoP (8.1 m² g⁻¹) was higher than that of H₂-NiMoP (4.2 m² g⁻¹). In addition, CHN analysis result showed no carbon in the CH₄/CO₂-NiMoP sample, indicating that no carbon deposition formed in the synthesis process.

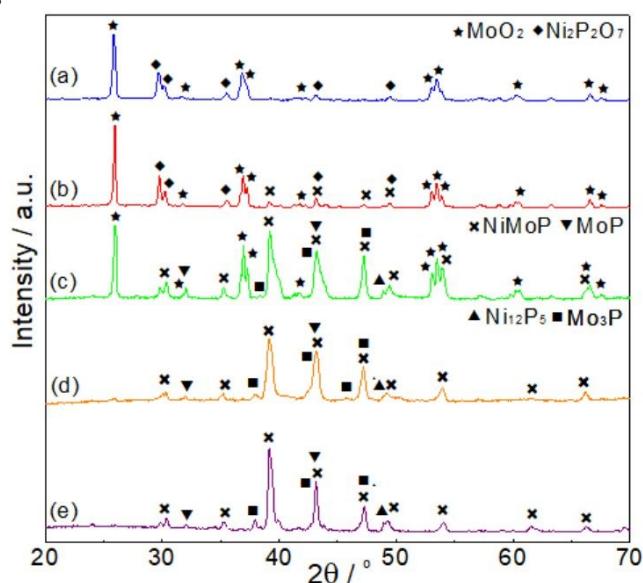


Fig. 6 XRD patterns of the products obtained from Ni₁Mo₁P₁ precursor with different time in CH₄/CO₂ at 900 °C. (a) 0 h, (b) 1 h, (c) 3 h, (d) 5 h and (e) 30 h.

The catalytic activity of the Ni₀Mo₁P₁, Ni₁Mo₁P₁ and Ni₁Mo₀P₁ precursors in DRM was investigated at 900 °C (Fig. 5). Among the three samples, the Ni₀Mo₁P₁ precursor exhibited the poorest activity with CH₄ and CO₂ conversions of ca. 7 and 10%, respectively within a period of 5 h. This was because the Ni₀Mo₁P₁ precursor cannot be reduced to MoP in CH₄/CO₂ gas mixture (see Fig. 1) and the MoOPO₄ product was almost not active for DRM. In the case of the Ni₁Mo₁P₁ and Ni₁Mo₀P₁ precursors, there was a rapid increase in CH₄ and CO₂ conversions in the initial period, which should be attributed to the in-situ formation of NiMoP from Ni₁Mo₁P₁ and Ni_xP from Ni₁Mo₀P₁, as suggested by XRD result (see Fig. 1). Note that the NiMoP (X_{CH₄}~83% and X_{CO₂}~87%) showed much higher CH₄ and CO₂ conversions than Ni_xP (X_{CH₄}~15% and X_{CO₂}~19%) when the reaction proceeded to reach its steady state. In addition, the high activity and selectivity (see Fig. S2) can be maintained over the catalyst for the duration of the experiment of 30 h and there was almost no change on the catalyst structure during the reaction from 5 to 30 h, as proved later by XRD. For the sake of

comparison, the DRM performance of NiMoP catalyst prepared in H₂ was also investigated under similar reaction conditions (see Figs. 5 and S2). It can be seen that the conversions over both CH₄/CO₂-NiMoP and H₂-NiMoP were far away from the values (X_{CH₄}~96% and X_{CO₂}~98%) at the reaction equilibrium.³¹ And the conversions over CH₄/CO₂-NiMoP were slightly higher (about 6%) than those over H₂-NiMoP under a WHSV=9000 cm³ g⁻¹ h⁻¹. When the WHSV was increased to 24000 cm³ g⁻¹ h⁻¹, the values of X_{CH₄} and X_{CO₂} for CH₄/CO₂-NiMoP were above 10% higher than those for H₂-NiMoP (Fig. S3). These results should be mainly attributed to its higher surface area and better particle dispersion (see Figs. 4 and S1).

Finally, in order to investigate the formation process of the NiMoP in CH₄/CO₂ gas mixture, some intermediate samples were characterized. Fig. 6 shows the XRD patterns of the products obtained from Ni₁Mo₁P₁ precursor with different time in CH₄/CO₂ at 900 °C. At 0 h, the precursor was transformed into a mixture phase of MoO₂ and Ni₂P₂O₇. This mixture should also include amorphous PO_x.²⁵ When the time increased to 1 h, a small amount of desired product NiMoP had appeared. With further increasing time, the intensity of the MoO₂ and Ni₂P₂O₇ peaks gradually decreased, and the Ni₁Mo₁P₁ precursor had been basically transformed into a single NiMoP phase at 5 h except a small quantity of Mo₃P and Ni₁₂P₅ phases.

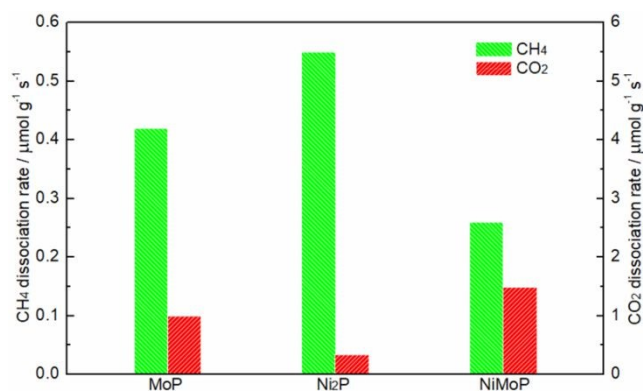


Fig. 7 Dissociation rates of CH₄ and CO₂ over MoP, Ni₂P and NiMoP catalysts. Reaction conditions: CH₄:Ar=1:50, CO₂:Ar=1:50, WHSV=30000 cm³ g⁻¹ h⁻¹, reaction time=10 min, reaction temperature=900 °C.

It had been confirmed from XRD that Ni₂P₂O₇ can be reduced easily to Ni_xP in CH₄/CO₂ (see Figs. 1 and 2). And the CH₄ and CO₂ dissociation studies (Fig. 7) indicated that the Ni₂P exhibited relatively high activity for CH₄ dissociation but relatively low activity for CO₂ dissociation. Therefore, it was reasonable to deduce that once the Ni_xP was formed, the Mo species might be reduced to Mo_xP by H₂ from CH₄ dissociation over Ni_xP. It was also found from Fig. S4 that the Ni phosphide can directly react with the Mo phosphide to form Ni_xMo_yP.²⁷ Thus, the formation process of NiMoP from Ni₁Mo₁P₁ precursor was proposed as follows: (i) the Ni_xP was formed in CH₄/CO₂; (ii) the Mo_xP was formed in Ni_xP-catalyzed CH₄ dissociation; (iii) the Ni_xP reacted with

Mo_xP to produce NiMoP. Note that the reaction products included a large amount of CO and H₂ besides H₂O, which can mitigate the hydrothermal sintering of phosphide particles and avoid carbon deposition on the surface.

5 Conclusions

In summary, we developed a novel in-situ approach to produce NiMoP catalyst in CH₄-CO₂ for the DRM. In this method, first the Ni_xP was formed and then the Mo_xP was formed in Ni_xP-catalyzed CH₄ dissociation. Finally, the Ni_xP reacted with Mo_xP to produce NiMoP. Compared with traditional H₂-TPR method, the reaction products included a large amount of CO and H₂ besides H₂O in this novel synthesis route, which can mitigate hydrothermal sintering of phosphide particles. The in-situ synthesized NiMoP in CH₄-CO₂ showed higher DRM activity than the NiMoP catalyst prepared in H₂, which should be mainly attributed to its higher surface area and better particle dispersion.

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Notes and references

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- 1 A.-M. Alexander and J.S.J. Hargreaves, *Chem. Soc. Rev.*, 2010, **39**, 4388-4401.
- 2 E.J. Popczun, J.R. McKone, C.G. Read, A.J. Biacchi, A.M. Wiltrout, N.S. Lewis and R.E. Schaak, *J. Am. Chem. Soc.*, 2013, **135**, 9267-9270.
- 3 K.Y. Yoon, Y. Jang, J. Park, Y. Hwang, B. Koo, J.-G. Park and T. Hyeon, *J. Solid State Chem.*, 2008, **181**, 1609-1613.
- 4 X.C. Jiang, Q.H. Xiong, S. Nam, F. Qian, Y. Li and C.M. Lieber, *Nano Lett.*, 2007, **7**, 3214-3218.
- 5 C. Stinner, R. Prins and Th. Weber, *J. Catal.*, 2001, **202**, 187-194.
- 6 R. Wang and K.J. Smith, *Appl. Catal. A*, 2009, **361**, 18-25.
- 7 Z. Yao, F. Luan, Y. Sun, B. Jiang and J. Song, *Catal. Sci. Technol.*, 2016, **6**, 7996-8004.
- 8 Y. Cui, Q. Liu, Z. Yao, B. Dou, Y. Shi and Y. Sun, *Int. J. Hydrogen Energy*, 2019, **44**, 11441-11447.
- 9 M. Zheng, Y. Shu, J. Sun and T. Zhang, *Catal. Lett.*, 2008, **121**, 90-96.
- 10 R. Cheng, Y. Shu, M. Zheng, L. Li, J. Sun, X. Wang and T. Zhang, *J. Catal.*, 2007, **249**, 397-400.
- 11 Z.W. Yao, H. Dong and Y. Shang, *J. Alloys Compd*, 2009, **474**, L10-13.
- 12 Y. Lv and X. Wang, *Catal. Sci. Technol.*, 2017, **7**, 3676-3691.
- 13 E.J. Popczun, C.G. Read, C.W. Roske, N.S. Lewis and R. E. Schaak, *Angew. Chem.*, 2014, **126**, 5531-5534.
- 14 L. Feng, H. Vrabel, M. Bensimon and X. Hu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5917-5921.
- 15 S. Burns, J.S.J. Hargreaves and S.M. Hunter, *Catal. Commun.*, 2007, **8**, 931-935.

- 60 16 Z. Yao, M. Li, X. Wang, X. Qiao, J. Zhu, Y. Zhao, G. Wang, J. Yin and H. Wang, *Dalton T.*, 2015, **44**, 5503-5509.
- 17 A. Wang, M. Qin, J. Guan, L. Wang, H. Guo, X. Li, Y. Wang and R. Prins, *Angew. Chem.*, 2008, **120**, 6141-6143.
- 18 V. Zuzaniuk and R. Prins, *J. Catal.*, 2003, **219**, 85-96.
- 65 19 R. Wang and K.J. Smith, *Appl. Catal. A*, 2009, **361**, 18-25.
- 20 B. Guichard, M. Roy-Auberger, E. Devers, C. Legensb and P. Raybaud, *Catal. Today*, 2008, **130**, 97-108.
- 21 S. Izhar and M. Nagai, *Catal. Today*, 2009, **126**, 172-176.
- 22 M. Nagai, T. Fukiage and S. Kurata, *Catal. Today*, 2005, **106**, 201-205.
- 70 23 J. Chen, Y. Yang, H. Shi, M. Li, Y. Chu, Z. Pan and X. Yu, *Fuel*, 2014, **129**, 1-10.
- 24 K Li, R Wang, J Chen, *Energy Fuels*, 2011, **25**, 854-863.
- 25 Z. Yao, J. Tong, X. Qiao, J. Jiang, Y. Zhao, D. Liu, Y. Zhang and H. Wang, *Dalton Trans.*, 2015, **44**, 19383-19391.
- 75 26 Z. Yao, G. Wang, Y. Shi, Y. Zhao, J. Jiang, Y. Zhang and H. Wang, *Dalton Trans.*, 2015, **44**, 14122-14129.
- 27 D. Ma, T.C. Xiao, S.H. Xie, W.Z. Zhou, S.L. Gonzalez-Cortes and M.L.H. Green, *Chem. Mater.*, 2004, **16**, 2697-2699.
- 28 P. Xiao, M.A. Sk and L. Thia, X.M. Ge, J.Y. Wang, K.H. Lim, R.J. Lim and X. Wang, *Energy Environ. Sci.*, 2014, **7**, 2624-2629.
- 80 29 A.W. Burns, A.F. Gaudette and M.E. Bussell, *J. Catal.*, 2008, **260**, 262-269.
- 30 Q. Guan, X. Cheng, R. Li and W. Li, *J. Catal.*, 2013, **299**, 1-9.
- 31 J. Li, C. Chen, D. Wang, W. Yao and S. Zhang, *Chem. Eng. Oil Gas*, 2015, **44**, 60-64.
- 85