Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name

COMMUNICATION

Efficient and Selective Hydrogenation of Biomass-Derived Furfural to Cyclopentanone Using Ru Catalysts

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ruiqi Fang,[a] Hongli Liu,[a] Rafael Luque,*[b] and Yingwei Li*[a]

The selective hydrogenation of furfural into cyclopentanone is an attractive transformation to advance in the sustainable synthesis of important chemicals from biomass. A supported Ru nanoparticle catalyst on an acidic MOF material (Ru/MIL-101) was designed for the highly active and selective conversion of furfural to cyclopentanone in aqueous media. Complete conversion of furfural with a selectivity higher than 96% were achieved within 2.5 h at 160 °C and 4.0 MPa H_2 pressure.

The demand of alternative energy sources grows quickly accompanied with a decrease in fossil-fuels worldwide. Biomass conversion to useful chemicals, materials and fuels has already proved to offer attractive possibilities to a more sustainable production of important commodities and specialty chemicals different from petrochemical sources.[1-4] Advantages of biomass to serve as resource for industrial fuels and feedstocks in the future,[5,6] as well as high-value compounds and chemical intermediates[7,8] include a wide availability, the presence of highly functionalised compounds containing O and N as well as well-known processing strategies (e.g. hydrodeoxygenation, fermentation, etc.). As an example, agricultural materials containing large quantities of cellulose including straw, corncobs, and oat hulls, typical lignocellulosic resources,[9-11] could be converted to important compounds such as furfural (FFA) via acid-catalytic dehydration.[12-14] Furfural is a highly useful chemical intermediate that can be further transformed into several valuable compounds[15-21] including cyclopentanone (CPO), furfural alcohol (FA), tetrahydrofurfuralalcohol (THFFA),[22] and 2-methylfuran (MF).[23]

Cyclopentanone (CPO) is a multifunctional reagent which plays a key role in applications for the production of insecticides, rubber chemicals, and pharmaceuticals. Typically, cyclopentanone is prepared by catalytic vapor-phase cyclisation of 1,6-hexanediol[24] or adipic esters,[25] or liquid-phase oxidation of cyclopentene with nitrous oxide.[26] From the viewpoint of sustainability and environmental soundness, the transformation of furfural into cyclopentanone received much interest in recent years.[27,28] Attempts to find suitable catalysts for the hydrogenation of furfural pointed to supported noble metals or Cu, Ni on various stable supports such as carbon, zeolites, alumina, or silica.[29-32] However, the target of high selectivity (>80%) at elevated conversion (>80%) is still a significant challenge in furfural conversion[15, 33-35] due to the production of large amounts of by-products including furfuryl alcohol, cyclopentanol and tetrahydrofurfuryl alcohol. Up to date, cyclopentanone yields are always lower than 76% even under harsh reaction conditions (e.g., 8 MPa hydrogen pressure). Consequently, there is a clear need to design highly efficient catalytic systems for selective furfural hydrogenation featuring high stability as well as greatly improved activity and selectivity.

In this contribution, we report the design of supported Ru catalysts on an acidic metal-organic framework (MOF) material for the selective hydrogenation of furfural to cyclopentanone. An unprecedented quantitative furfural conversion to cyclopentanone (complete conversion, 96% selectivity to cyclopentanone) could be achieved under optimised conditions for 3%Ru/MIL-101 (Ru nanoparticles supported on MIL-101). The catalyst was also proved to be highly recyclable and may be reused without any significant loss of reactivity under the optimised investigated conditions.

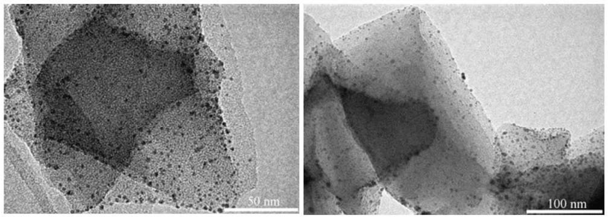


Figure 1. TEM images of 3% Ru-MIL-101 at different magnifications.

MIL-101(Cr) (MIL: Matériaux de l'Institut Lavoisier) was employed in this work, featuring a large BET surface area (ca. 3000 m^2 g^{-1}), pore size (ca. 3 nm) and an acceptable thermal stability up to ca. 310 °C.[36] Powder XRD patterns of Ru loaded materials (Fig. S1) matched well with those of parent MIL-101,[37] confirming a well

---

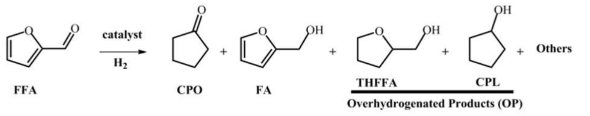
[a] State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640 (China). E-mail: liyw@scut.edu.cn

[b] Departamento de Química Orgánica. Universidad de Córdoba, Edif. Marie Curie, Ctra Nnal IVa, Km 396, E14014, Córdoba (Spain).E-mail: q62alsor@uco.es

† Electronic Supplementary Information (ESI) available: Experimental, catalyst characterization, and additional reaction results. See DOI: 10.1039/x0xx00000x

preserved MIL-101 structure after Ru incorporation by a simple incipient wetness impregnation method.[38] The absence of diffraction lines for Ru could be attributed to the small size of Ru particles and/or absence of high crystallinity for all samples as well as the low metal loading (under 5 wt.%). The noticeable reduction in nitrogen adsorption with respect to pristine MIL-101 could be related to pore blockage by highly dispersed metal nanoparticles migrated to the pores and at the surface of the material (Fig. S2 and Table S1). TEM micrographs generally indicated the presence of well dispersed Ru nanoparticles with NP sizes of ca. 4-5 nm (Fig. 1), without any significant formation of aggregates. XPS analysis (Fig. S3) also confirmed the presence of Ru^0 in the materials as clearly demonstrated by a band at 461.9 eV, characteristic of zerovalent Ru species.[39]

Table 1. Hydrogenation of FFA to CPO over different catalysts. [a]



Entry	Catalyst	Conv (%)	Selectivity (%)				CPO yield/ isolated yield (%)	C balance (%)
			CPO	FA	OP	others		
1	–	-	-	-	-	-	-	-
2	MIL-101	-	-	-	-	-	-	-
3	1 wt% Ru/MIL-101	46	60	22	-	18	28/23	96
4	2 wt% Ru/MIL-101	93	78	16	1	5	73/69	97
5	3 wt% Ru/MIL-101	>99	96	1	2	1	96/94	98
6	4 wt% Ru/MIL-101	95	79	2	18	1	75/71	97
7	5 wt% Ru/MIL-101	90	68	1	30	1	61/58	97
8	3 wt% Ru/C	72	40	46	-	14	29/25	96

[a] Conditions: FFA (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 160 °C, 4 MPa H_2, 2.5 h. Other products included THFA, 2-MTHFA, 2-MFA, etc.

Upon characterization completion, the catalyst was subsequently tested in the aqueous hydrogenation of furfural (FFA) in an autoclave at hydrogen pressure of 4 MPa and temperature of 160 °C. As shown in Table 1, blank reactions (in the absence of catalyst or even in the presence of parent MIL-101) gave essentially no reactivity (Table 1, entries 1-2). Ru loading significantly affected FFA conversion and products selectivity (entries 3-7). Results of FFA hydrogenation pointed to an optimized performance of 3% Ru/MIL-101, which afforded a complete FFA conversion with 96% selectivity to CPO (entry 5). Selectivity to CPO decreased with a concomitant increase in selectivity to over-hydrogenation products with a further increase in Ru mass fraction. These results may suggest some aggregation of Ru particles on the MIL-101 surface at high metal loadings, in a similar way to that previously reported for metal nanoparticles supported on MIL-101.[40] As shown in Fig. S4, a significant aggregation of Ru nanoparticles was observed for 4 wt% Ru and 5 wt% Ru/MIL-101.

For comparative purposes, a Ru catalyst supported on active carbon (Ru/C) was prepared and its activity tested in the reaction under identical conditions. The observed conversion of FFA and CPO selectivity for Ru/C were remarkably inferior (Table 1, entry 8), with a considerable production of furfuryl alcohol (FA, ca. 46%) under the investigated conditions as compared to Ru/MIL-101 catalyst. These results clearly illustrate the significance of the support in the hydrogenation reaction.

The reaction profile for the reaction catalysed with the optimum system (3% Ru/MIL-101) was further followed at 160 °C and 4 MPa H_2 (Fig. 2). These experiments showed that FFA conversion steadily increased with time, fully depleting FFA after 2.5 hours. The selectivity to CPO also increased at the same time. The selectivity to furfuryl alcohol (FA) was as high as 91% after 10 min of reaction but significantly dropped with the evolution of the reaction to only product traces after 2.5 h. These results suggested that furfural alcohol is likely to be an intermediate for the formation of CPO. Cyclopentanol (CPL) was detected as over-hydrogenated product of CPO after times of reaction longer than 1 hour.

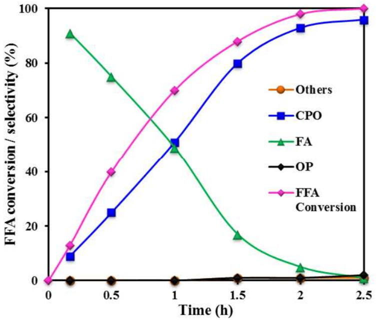


Figure 2. FFA conversion and products selectivity as a function of reaction time. Reaction conditions: FFA (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 160 °C, 4 MPa H_2.

Different reaction temperatures were subsequently screened (Fig. 3a), with observed high FFA conversions (>70%) even at 120 °C. Interestingly, CPO could only be detected after 0.5 h of reaction at 120 °C, with main reaction products being FA and tetrahydrofurfural alcohol (THFFA) (total selectivity > 85%) at FFA conversions lower than 30%. As the temperature increased to >140 °C, the reaction rate significantly increased with improved CPO selectivities (reduced selectivities to FA and related products were obtained). Over-hydrogenation products (i.e., CPL and THFFA) were mostly observed at reaction temperatures higher than 180 °C.

We also investigated the effect of H_2 pressure on FFA hydrogenation at the optimized temperature of 160 °C (Fig. 3b). An increase in H_2 pressure led to an enhancement in FFA conversion. Similarly, higher selectivities to over-hydrogenation products (e.g. cyclopentanol) were observed at hydrogen pressures over 4 MPa.

The long-term stability of heterogeneous catalysts can be particularly challenging under aqueous processing conditions and moderate to high temperatures. Consequently, the prospects to reuse Ru/MIL-101 were subsequently explored. Results from Fig. 4 clearly demonstrate that the catalytic system could be reused up to 6 times without any significant decrease in conversion and selectivity to the target product. Hot filtration experiments were also conducted to verify whether reaction was truly heterogeneous. In this case, the solid catalyst was filtered from the ongoing reaction solution after 10 min and subsequently reutilized in analogous reaction runs with fresh substrates.

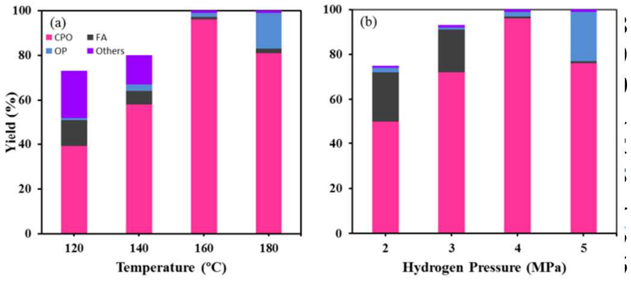


Figure 3. Effect of reaction temperature and hydrogen pressure on FFA conversion and product selectivity over 3% Ru/MIL-101. Reaction conditions: FFA (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 2.5 h; (a) 4 MPa H_2, (b) 160 °C.

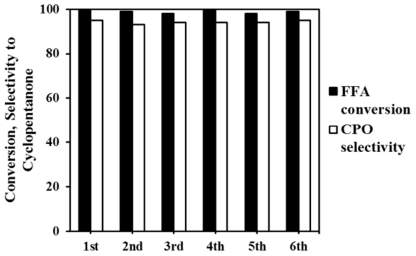


Figure 4. Reuses of the 3% Ru/MIL-101 catalyst in FFA hydrogenation. Reaction conditions: FFA (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 160 °C, 4 MPa H_2, 2.5 h.

Furthermore, the reaction mixture after catalyst filtration was further investigated to observe any changes in conversion with time due to metal leached into solution. No metal leaching was observed by AAS analysis into the liquid phase during/after the reaction, with the filtrate showing no further FFA conversion in the absence of catalyst (Fig. S5). XRD characterization results (Fig. S1) confirmed that the crystalline structure of the catalyst was mostly maintained even after several reuses.

Hydrogenation of *α,β*-unsaturated aldehydes has been the subject of extensive investigations in recent years,[41] with both experimental and theoretical studies pointing out that the catalytic performance can be critically affected by adsorption profiles and adsorbed compounds on the surface of the catalyst.[42,43] Generally speaking, the reaction is more likely to take place when the reactant is directly bonded to the surface metal atom.[44] For instance, hydrogenation of acrolein over Pt primarily gives propanal via C=C hydrogenation, as the Pt surface strongly adsorbs acrolein from the two carbon atoms of the C=C bond.[45] Substituents on the C=C bond may also greatly affect the adsorption model. As for crotonaldehyde, the methyl group on the C=C bond strengthens steric hindrance and makes an easier adsorption via C=C and C=O bonds.[46,47] However, molecules containing two C=C bonds and one C=O bond in the same plane such as furfural and HMF are likely to have a much different adsorption on the metal surface.[48] In this case, the two C=C bonds are strongly adsorbed on the metal surface, making the molecular plane parallel to the metal surface. Thus, the C=O bond is close to the metal surface which will also be coordinated to the metal.[49] As a result, C=O selective hydrogenation is in principle easier for furfural as compared to crotonaldehyde. On the other hand, the aromatic nature of the furan ring could reduce C=C bond hydrogenation activity while promoting C=O hydrogenation selectivity.[50]

Based on these premises, a number of adsorption studies were conducted and profiles were recorded by DRIFTs (Fig. 5). DRIFT studies of furfural adsorption over Ru/MIL-101 provided a number of interesting findings as compared to parent Ru/MIL-101. Compared to the rather clean and distinctive spectra for Ru/MIL-101, the adsorption of furfural gave rise to various fine bands in the IR spectra indicative of weak energy interactions in the range of 1300 to 2100 cm^{-1}.[51] Bands in the 1700-1500 cm^{-1} are present at different desorption temperatures but the main broad band (ca. 1700-1650 cm^{-1}) attributed to chemisorbed furfural[51,52] comprises of two components which gradually change with desorption temperature from 25 to 200 °C towards lower frequencies (Fig. 5). This is often indicative of electron-donation to the coordinated carbon from the C=O bond (decreasing the double bond character of the carbonyl group). A weak shoulder at 1730-1750 cm^{-1} generally associated with physisorbed furfural[51,52] gradually disappears at increasing temperatures from 100 to 300 °C (Fig. 5). Bands at associated with the vibrations of the furan ring double bond may be present in the 1500-1450 cm^{-1} range but these cannot be clearly visualized in the DRIFT spectra due to the background signal. In any case, these adsorption studies clearly pointed out a strong chemisorption of FFA on the Ru/MIL-101 support even at relatively high temperatures (>150 ºC), similar to those selected for the hydrogenation reaction.

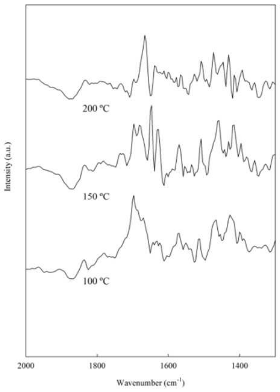


Figure 5. DRIFT desorption studies of adsorbed furfural on 3% Ru/MIL-101.

Furthermore, the observed shift to lower frequencies of the characteristic furfural chemisorption in the experiments can also be related to a lower double bond character of the adsorbed aldehyde group in furfural due to interaction with the support which will strongly favor C=O as compared to C=C hydrogenation.

A plausible reaction mechanism depicted in Fig. 6 from adsorption studies may point out that furfural was firstly converted into furfuryl alcohol (FA) via C=O hydrogenation under hydrogen atmosphere. The selectivity to the key intermediate FA was as high as 91% after 10 min of reaction, as shown in Fig. 2. The significant drop in FA selectivity (Fig. 2) with reaction time indicated that FA was subsequently converted to 4-hydroxy-2-cyclopentenone (HCP) on the Lewis acidic Cr^{3+} sites of MIL-101 (ca. 2 mmol g^{-1})[38] via piancatelli rearrangement as previously reported.[53] HCP was immediately hydrogenated and dehydrated to form 2-cyclopentenone that underwent further hydrogenation to provide CPO as target product. The two reaction steps were really fast because of the high reactivity of HCP and 2-cyclopentenone in the present system. The over-hydrogenation of the C=O bond in CPO could be effectively suppressed over the Ru/MIL-101, a fact that is suggested to be related to a Lewis acid-base interaction in the catalyst,[38,54] leading to the extremely high selectivity to CPO.

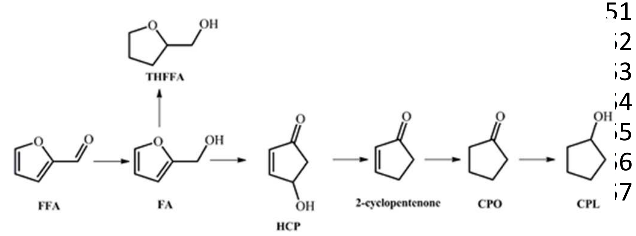
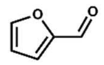
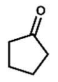
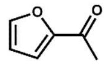
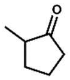
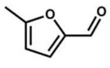
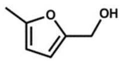
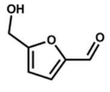
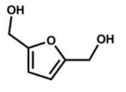


Figure 6. The possible reaction pathway of FFA hydrogenation in water over Ru/MIL-101.

Table 2. Hydrogenation of furan derivatives[a]

Entry	Substrate	Product	Yield (%)
1			96
2			82
3			52
4			67

[a] Reaction conditions: substrate (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 160 °C, 4 MPa H_2, 2.5 h.

Various furan derivatives were also tested in the hydrogenation reaction using 3%Ru/MIL-101 as optimum catalyst. Using 2-acetylfuran as reactant, 2-methyl-cyclopentanone could be obtained in 82% yield (Table 2, entry 2). However, when methyl furfural or 5-hydroxymethyl furfural (HMF) were used as substrates, the rearrangement reaction of the furan ring could not take place (Table 2, entries 3 and 4), revealing that Lewis acid sites were not favourable for the rearrangement of 5-substituted furan derivatives.[53]

Conclusions

Ru nanoparticles have been heterogeneously supported on MOF MIL-101 featuring unique acidic properties. The novel Ru catalyst exhibited a high activity and exceptional selectivity in the aqueous hydrogenation of furfural, an interesting biomass-derived platform chemical. A complete furfural conversion with a CPO selectivity >96% could be achieved within 2.5 h at 160 °C and 4.0 MPa H_2 pressure. The high catalytic performance of the proposed system could be attributed to the special structural and acid properties of MIL-101, able to provide an optimum support for a homogeneous dispersion of Ru nanoparticles in the system as well as Lewis acid sites for the required dehydration step of 4-hydroxy-2-cyclopentenone (HCP). The heterogeneous catalyst can be easily recovered by filtration and reused multiple times without any substantial change in activity and product selectivity. The highly efficient hydrogenation of furfural using stable and reusable catalysts may open new perspectives for the application of MOF materials in biomass transformations.

Acknowledgements

This work was supported by the NSF of China (21322606 and 21436005), the Doctoral Fund of Ministry of Education of China (20120172110012), the Guangdong Natural Science Foundation (2013B090500027 and 10351064101000000), and the Fundamental Research Funds for the Central Universities.

Notes and references

1 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502.
2 M. Chatterjee, T. Ishizaka and H. Kawanami, *Green Chem.*, 2014, **16**, 1543-1551.
3 K. Pupovac and R. Palkovits, *ChemSusChem,* 2013, **6**, 2103-2110.
4 M. Zhao, S. Ou and C. Wu, *Acc. Chem. Res.,* 2014, **47**, 1199-1207.
5 C. Xu, R. A. D. Arancon, J. Labidi and R. Luque, *Chem. Soc. Rev.,* 2014, **43**, 7485-7500.
6 L. Hu, G. Zhao, W. Hao, X. Tang, L. Lin and S. Liu, *RSC Adv.,* 2012, **2**, 11184-11206.
7 J. G. Stevens, R. A. Bourne, M. V. Twigg and M. Poliakoff, *Angew. Chem. Int. Ed.,* 2010, **49**, 8856-8859.
8 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem. Int. Ed.,* 2007, **46,** 7164-7183.

9 T. D. Matson, K. Barta, A. V. Iretskii and P. C. Ford, *J. Am. Chem. Soc.,* 2011, **133**, 14090-14097.
10 V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler and D. G. Vlachos, *J. Am. Chem. Soc.,* 2013, **135**, 3997-4006.
11 M. Stocker, *Angew. Chem. Int. Ed*., 2008, **47**, 9200-9211.
12 R. Karinen, K. Vilonen and M. Niemelä, *ChemSusChem,* 2011, **4**, 1002-1016.
13 J. B. Binder, J. J. Blank, A. V. Cefali and R. T. Raines, *ChemSusChem,* 2010, **3**, 1268-1272.
14 K. Yan and A. Chen, *Energy,* 2013, **58**, 357-363.
15 J. P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem,* 2012, **5**, 150-166.
16 Y. Yang and C. O. Hernández, *Appl. Catal. B: Environ.,* 2014, **145**, 91-100.
17 C. Aellig and I. Hermans, *ChemSusChem,* 2012, **5**, 1737-1742.
18 D. Sudipta, S. Basudeb and R. Luque, *Bioresour. Technol.,* 2014, **9**, 65-75.
19 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.,* 2014, **114**, 1827-1870.
20 Y. B. Huang, Z. Yang, M. Y. Chen, J. J. Dai, Q. X. Guo and Y. Fu, *ChemSusChem,* 2013, **6**, 1348-1351.
21 E. J. García-Suárez, A. M. Balu, M. Tristany, A. B. García, K. Philippot and R. Luque, *Green. Chem.,* 2012, **14**, 1434-1439.
22 V. V. Ordomsky, J. C. Schouten, J. van der Schaaf and T. A. Nijhuis, *Appl. Catal. A: Gen.,* 2013, **451**, 6-13.
23 D. Scholz, C. Aellig and I. Hermans, *ChemSusChem,* 2014, **7**, 268-275.
24 Y. Nakagawa and K. Tomishige, *Chem. Commun.,* 2010, **12**, 154-156.
25 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature,* 2007, **447**, 982-986.
26 T. Akashi, S. Sato, R. Takahashi, T. Sodesawa and K. Inui, *Catal. Commun.,* 2003, **4**, 411–416.
27 K. A. Dubkov, G. I. Panov, E. V. Starokon and V. N. Parmon, *React. Kinet. Catal. Lett.,* 2002, **77,** 197–205.
28 J. van Puten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. De Vries, *Chem. Rev.,* 2013, **113**, 1499-1597.
29 J. Gong and R. Luque, *Chem. Soc. Rev.,* 2014, **43**, 7466-7468.
30 T. Suzuki, T. Yokoi, R. Otomo, J. N. Kondo and T. Tatsumi, *Appl. Catal. A: Gen.,* 2011, **408**, 117–124.
31 M.Hronec and K. Fulajtarová, *Catal. Commun.,* 2012, **24**, 100-104.
32 H. Zhu, M. Zhou, Z. Zeng, G. Xiao and R. Xiao, *Korean J. Chem. Engineer.,* 2014, **31**, 593-597.
33 M. Hronec and K. Fulajtarová, T. Liptaj, *Appl. Catal. A: Gen.,* 2012, **104**, 437–438.
34 Y. Yang, Z Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chem*., 2013, **15**, 1932-1940.
35 Y. Nakagawa, M. Tamura and K. tomishige, *ACS Catal*., 2013, **3**, 2655-2668.
36 Y. Pan, B. Yuan, Y. W. Li and D. He, *Chem. Commun.*, 2010, **46**, 2280–2282.
37 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science,* 2005, **309**, 2040-2042.
38 H. L. Liu, Y. W. Li, R. Luque and H. F. Jiang, *Adv. Synth. Catal.,* 2011, **353**, 3107-3113.
39 K. Qadir, S. H. Joo, B. S. Mun, D. R. Butcher, J. R. Renzas, F. Aksoy, Z. Liu, G. A. Somorjai and J. Y. Park, *Nano Lett.,* 2012, **12**, 5761-5768.
40 A. M. Balu, C. S. K. Lin, H. Liu, C. Vargas, Y. Li and R. Luque, *Appl. Catal. A: Gen.,* 2013, **455**, 261-266.
41 W. Yu, M. D. Porospff and J. G. Chen, *Chem. Rev.,* 2012, **112**, 5780-5817.
42 J. W. Medlin, *ACS Catal*., 2011, **1**, 1284-1297.
43 R. Ranjan, S. Thust, C. E. Gounaris, M. Woo, C. A. Floudas, M. V. Keitz, K. J. Valentas, J. Wei and M. Tsapatsis, *Microporous Mesoporous Mater.,* 2009, **122**, 143-148.
44 K. Zhang, M. Agrawal, J. Harper, R. Chen and W. J. Koros, *Ind. Eng. Chem. Res.,* 2011, **50**, 14055-14060.
45 F. Delbecs and P. Sautet, *J. Catal*., 2002, **211**, 398-406.
46 J. Haubrich, D. Loffreda, F. Delbecq, P. Sautet, Y. Jugnet, A. Krupski, C. Becker and K. Wandelt, *J. Phys. Chem. C.,* 2008, **112**, 3701-3718.
47 J. Haubrich, D. Loffreda, F. Delbecq, P. Sautet, A. Krupski, C. Becker and K. Wandelt, *J. Phys. Chem. C.,* 2009, **113**, 13947-13967.
48 S. Sitthisa, T. Sooknoi, Y. Ma, P. B. Balbuena and D. E. Resasco, *J. Catal.,* 2011, **277**, 1-13.
49 Y. Nakagawa, H. Nakazawa, H. Watanabe and K. Tomishige, *ChemCatChem,* 2012, **4***,* 1791-1797.
50 R. Rao, A. Dandekar, R. T. K. Baker and M. A. Vannice, *J. Catal*., 1997, **171**, 406-419.
51 G. L. Dimas-Rivera, J. Rivera de la Rosa, C. J. Lucio-Ortiz, J. A. De los Reyes Heredia, V. Gonzalez Gonzalez and T. Hernandez, *Materials,* 2014, **7**, 527-541.
52 W. Zhang, Y. Zhu, S. Niu and Y. Li, *J. Mol. Catal. A: Chem.,* 2011, **335**, 71–81.
53 G. Veits, D. Wenz and J. Alaniz, *Angew. Chem. Int. Ed.* 2010, **49**, 9484-9487.
54 H. Liu, Z. Li and Y. W. Li, *Ind. Eng. Chem. Res.*, 2015, **54**, 1487−1497.