Heterogeneous Beckmann Rearrangements Catalyzed by a Sulfonated Imidazolium Salt of Phosphotungstate

Xuan Zhang · Dan Mao · Yan Leng · Yu Zhou · Jun Wang

Received: 1 September 2012/Accepted: 8 November 2012/Published online: 27 November 2012 © Springer Science+Business Media New York 2012

Abstract The heteropolyanion-based ionic liquid (IL) material [MIMPS]₃PW₁₂O₄₀, propane sulfoacid-functionalized imidazolium salt of phosphotungstate, was used as a solid catalyst for liquid-phase Beckmann rearrangements of ketoximes in the presence of zinc chloride. The resultant liquid–solid biphasic rearrangement reaction of cyclohexanone oxime shows a high yield 83 % with good recyclability. The testing of control catalysts, reaction conditions, oxime substrates, and recycling property were carried out and the results are discussed.

Keywords Ionic liquid · Beckmann rearrangement · Cyclohexanone oxime · Caprolactam · Phosphotungstate

1 Introduction

Beckmann rearrangements are a class of very important organic reactions that convert oximes into amides [1]. Rearrangement of cyclohexanone oxime has been applied in petrochemical industry to synthesize ε -caprolactam, a precursor of nylon-6 [2]. Various catalysts are used for Beckmann rearrangements

Electronic supplementary material The online version of this article (doi:10.1007/s10562-012-0939-5) contains supplementary material, which is available to authorized users.

X. Zhang · D. Mao · Y. Zhou · J. Wang (⊠) State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China e-mail: junwang@njut.edu.cn

Y. Leng

School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, People's Republic of China

conducted in either vapour or liquid phase [3]. For a vapour phase reaction, solid acid catalysts including boric acid, silica– alumina and zeolite demand a high reaction temperature to exhibit good activities, which has drawbacks of quick deactivation and highly energy-consuming [4]. Therefore, a lowtemperature liquid-phase rearrangement has attracted much research interest. Oleum has been used as the catalyst/medium for rearrangement of cyclohexanone oxime, giving a high yield of ε -caprolactam, but the system shows disadvantages of heavy corrosion and a large amount of by-product ammonium sulphate [5]. To overcome these problems, great efforts have been made, including the use of acetonitrile [6, 7], ionic liquids (ILs) [8, 9] and critical water [10, 11] as effective solvents.

Ionic liquids are well-known solvents/catalysts due to structural versatility, high thermal stability, alterable solubility, and negligible volatility [12–14]. Various Lewis acidic ILs, such as of AlCl₃, TiCl₄, SnCl₄, BF₃, PCl₅, and POCl₃, have used as catalysts for Beckmann reaction [9, 15]. Also, Brønsted acidic IL catalysts are employed for this reaction. For example, Guo et al. [16] used caprolactambased Brønsted acidic ILs as solvents/catalysts to synthesize ε-caprolactam without reporting catalyst recycling properties. Liu et al. [17] developed an active recyclable sulfoacidtethered di-imidazolium IL catalyst for converting aromatic oximes in the presence of zinc chloride; nevertheless, the catalyst was inactive for the substrate of acetoxime. Turgis et al. [5] prepared a reusable IL with sulfonic acid-functionalized cation and hydrogen sulfate anion, and revealed that the Brønsted acidity of sulfoacid groups in cation was responsible for Beckmann reaction, but the good activity could be observed only when the IL was used in an excess amount with respect to oxime.

Heteropolyacids (HPAs) are widely applied catalysts for organic transformations, but seldom used for Beckmann rearrangement [18]. The few examples include the SiMCM41-supported phosphotungstic acid catalyst for the vapour phase synthesis of ε -caprolactam [19] and the HPA cesium salt catalyst for liquid-phase rearrangement of aromatic oximes [20]. Noticeably, organic IL-cation salts of HPAs usually have high melting points due to the large volume and high valence of HPA-anions [21, 22], and these HPA–IL ionic compounds are novel catalytic materials [23]. Recently, we have prepared a series HPA–IL catalysts for organic reactions [24–30]. Typically, we synthesized and characterized a IL-cation phosphotungstate [MIMPS]₃PW₁₂O₄₀ [24]. Considering the Brønsted acidity, solid nature, and insolubility of this organic HPA salt in this study, we try it as the catalyst for Beckmann rearrangement (Scheme 1). Various control catalysts, reaction conditions, and substrates are investigated.

2 Experimental

2.1 Preparation of [MIMPS]₃PW₁₂O₄₀ and Control Catalysts

Preparation and characterization for phosphotungstate salts of sulfonated IL-cations have been reported in our previous work [24]. For preparing [MIMPS]₃PW₁₂O₄₀, methylimidazole (0.11 mol) and 1,3-propane sulfone (0.1 mol) were dissolved in anhydrous toluene (25 mL), with a stirring at 50 °C for 24 h under nitrogen atmosphere. The resulting white precipitate (MIMPS) was filtered and washed with diethyl ether and then dried in vacuum. Then, MIMPS (0.06 mol) was added to an aqueous solution of H₃PW₁₂O₄₀ (0.02 mol), and the mixture was stirred at room temperature for 24 h. Finally, water was removed in vacuum to give [MIMPS]₃PW₁₂O₄₀ as a solid. [3-(1-Methylimidazolium-3-yl) propane-1-sulfonate]₃PW₁₂O₄₀ and [MIMPS]₂HPW₁₂O₄₀ were prepared with controlled molar ratios of cation and anion. Other control samples of [3-butyl-1-methylimidazolium]₃ PW₁₂O₄₀, [(3-sulfonic acid)propylpyridinium]₃PW₁₂O₄₀, and [(3-sulfonic acid)propyltriethylammonium]₃PW₁₂O₄₀ were also prepared accordingly, which are designated as [BMIM]₃PW₁₂ O₄₀, [PyPS]₃PW₁₂O₄₀ ,and [TEAPS]₃PW₁₂O₄₀, respectively.

2.2 Procedures for Beckmann Rearrangement Reactions

Oxime (2 mmol), catalyst (0.2 mmol), ZnCl₂ (0.2–0.6 mmol), and 5 mL solvent were added into a 25 mL round-bottom flask

with a magnetic stirrer and a condenser. Then, the reaction was controlled to proceed for 1-6 h at 90 °C. At the end of the reaction, the resulting mixture was cooled and the liquid phase was decanted for analysis. When using MeCN, DMF, 1,4-dioxane, and toluene as the solvents, respectively, the systems were heterogeneous throughout the reaction processes. However, the solvent ethanol caused a homogeneous reaction at the working temperature, and after reaction with the reaction mixture cooled down to room temperature the catalyst deposited. Quantitative analyses for the reacted solution the solid catalyst removed were conducted with Shimadzu GC-2014 equipped with a FID detector and a capillary column (SE-30; 50 m \times 0.25 mm \times 0.3 μ m). Every amide product from the rearrangement of an oxime substrate was confirmed in the gas chromatogram by the corresponding pure amide compound. For the Beckmann rearrangement of cyclohexanone oxime, only cyclohexanone derived from the deoximation of cyclohexanone oxime was detected as the by-product besides the major rearrangement product ɛ-caprolactam. The conversion of cyclohexanone oxime (Conv. %) and selectivity for ε-caprolactam (Sel. %) were calculated as Conv. $\% = (\text{mol } \varepsilon \text{-caprolac-}$ tam + mol cyclohexanone) / mol initial cyclohexanone oxime. Selectivity $\% = \text{mol } \epsilon$ -caprolactam / (mol ϵ -caprolactam + mol cyclohexanone). For Beckmann rearrangements of other oxime substrates, the GC yields for amide products were obtained by adding the internal standard cyclohexane.

3 Results and Discussion

3.1 Beckmann Rearrangement of Cyclohexanone Oxime over Various Heteropolyanion-based ILs Catalysts

Cyclohexanone oxime is used as a probe molecule to examine the feasibility of the heteropolyanion-based ILs catalysts for Beckmann rearrangements in the presence of ZnCl₂. The results are summarized in Table 1. Without any catalyst, the reaction gave no product (entry one), while ZnCl₂ alone did not show any catalytic activity (entry two). The catalyst [MIMPS]₃PW₁₂O₄₀ gave a low conversion of cyclohexanone oxime 22 % in the absence of ZnCl₂ (entry three). The classical pure HPA catalyst $H_3PW_{12}O_{40}$ in the presence of ZnCl₂ gave a conversion 89 % and selectivity 83 % (entry four). Interestingly, with both [MIM-PS]₃PW₁₂O₄₀ and ZnCl₂, the system exhibited a full conversion 100 % with a high selectivity for ε-caprolactam 83 % (entry five). Cyclohexanone, derived from deoximation of cyclohexanone oxime, is the only by-product detected by GC. The observation that ZnCl₂ acts as a cocatalyst is consistent with previous reports [7, 31].

Table 1 Beckmann rearrangement of cyclohexanone oxime over various HPA–IL catalysts in the presence of $ZnCl_2$

Entry	Catalyst	Conv./ %	Sel./ %
1 ^a	Non-catalyst	Trace	_
2 ^b	$ZnCl_2$	Trace	_
3 ^c	[MIMPS] ₃ PW ₁₂ O ₄₀	22	45
4	$H_{3}PW_{12}O_{40}$	89	83
5	[MIMPS] ₃ PW ₁₂ O ₄₀	100	83
6	[MIMPS] _{2.5} H _{0.5} PW ₁₂ O ₄₀	95	83
7	[MIMPS] ₂ HPW ₁₂ O ₄₀	86	84
8	[BMIM] ₃ PW ₁₂ O ₄₀	Trace	_
9	[PyPS] ₃ PW ₁₂ O ₄₀	89	74
10	[TEAPS] ₃ PW ₁₂ O ₄₀	90	76

Reaction conditions: cyclohexanone oxime 2 mmol, catalyst 0.2 mmol, ZnCl_2 0.6 mmol, MeCN (solvent) 5 mL, 90 °C, 1 h

 $^a\,$ Without [MIMPS]_3PW_{12}O_{40} and ZnCl_2

^b With ZnCl₂, without [MIMPS]₃PW₁₂O₄₀

^c With [MIMPS]₃PW₁₂O₄₀, without ZnCl₂

When the loading of the sulfoacid-tethered cation MIMPS in phosphotungstate salts was reduced, the resultant samples, $[MIMPS]_{2.5}H_{0.5}PW_{12}O_{40}$ and $[MIMPS]_2$ HPW₁₂O₄₀, showed gradually lower conversions down to 86 % (entries six and seven). One may thus draw that the acidity of the sulfonic acid groups in the cation moiety must have acted as the active centers for the rearrangement. This is further confirmed by the data in entry eight that the non-sulfonic acid counterpart, $[BMIM]_3PW_{12}O_{40}$, was inactive. Moreover, pyridinium- and ammonium-based analogues, $[PyPS]_3PW_{12}O_{40}$ and $[TEAPS]_3PW_{12}O_{40}$ (entries nine and ten), presented lower conversion and selectivity than the imidazolium-based $[MIMPS]_2HPW_{12}O_{40}$. The higher activity of the latter may stem from the additional acidity of 2-position hydrogen of the imidazole ring [32].

3.2 Influence of Reaction Conditions for Rearrangement of Cyclohexanone Oxime over [MIMPS]₃PW₁₂O₄₀

Figure 1 shows the influence of reaction time on conversion and selectivity for Beckmann rearrangement of cyclohexanone oxime over the HPA–IL catalyst [MIMPS]₃ PW₁₂O₄₀. It can be seen that the conversion increased quickly at early reaction period, and then reached to 100 % at 1 h. The selectivity for ε -caprolactam showed a same trend as the conversion, attaining a constant high value 83 % after 45 min. At the early reaction stage, the lower selectivity for ε -caprolactam is due to the formation of a considerable amount of cyclohexanone caused by deoximation reaction on fresh acidic sites; afterwards, more and



Fig. 1 Effect of reaction time on Beckmann rearrangement of cyclohexanone oxime



Fig. 2 Effect of reaction temperature on Beckmann rearrangement of cyclohexanone oxime

more created basic ε -caprolactam product should at least contaminate at part of the strong acidic sites and thus remarkably, hindered the side reaction of deoximation.

Effect of reaction temperature is shown in Fig. 2. As reaction temperature rose from 50 to 90 °C, both conversion and selectivity increased significantly. A full conversion was got at 90 °C. At the higher temperature 110 °C, the conversion 100 % could be obtained within a shorter time 45 min. Nevertheless, a lower selectivity for ε -caprolactam was observed, mostly due to the formation of condensation products from ketone by the deoximation at such a high temperature [33]. Therefore, 90 °C is selected as the optimal temperature.

Influence of the amount of cocatalyst $ZnCl_2$ added in reaction is displayed in Fig. 3. When the reaction proceeded without $ZnCl_2$, very low conversion 22 % and low selectivity 45 % were detected. With increasing the amount of $ZnCl_2$ up to 0.6 mmol, both conversion and selectivity increased, where a full conversion of cyclohexanone oxime was attained. A further increase of $ZnCl_2$ to 1 mmol led to only a slight increase in selectivity by 3 %. Thus, the preferential amount of $ZnCl_2$ is 0.6 mmol, and in this case, the molar ratio of [MIMPS]₃PW₁₂O₄₀ to ZnCl₂ is 1:3.

In the previously proposed mechanism for the rearrangement of cyclohexanone oxime catalyzed by an acidic catalyst, the nitrogen of cyclohexanone oxime is first protonated by the Brønsted acid site of catalyst with the creation of the nitrilium intermediate [34], then O-protonated oxime is generated from the 1,2-H-shift route by the proton transfer from nitrogen to oxygen [35, 36]. On the other hand, coordination of a Lewis acid to a Brønsted acid has been revealed to increase significantly the original acidity of the latter [37]. It is thus suggest that the co-catalytic function of the Lewis acid ZnCl₂ is to increase the overall acidity of the reaction system catalyzed by the Brønsted acidic [MIMPS]₃PW₁₂O₄₀, promoting the protonation route with comparatively a high activation energy [38]. Additionally, the previous study [7] conjuncted the form of a reaction intermediate of seven-ring nitrilium cation from the chelation of ZnCl₂ with the nitrogen of cyclohexanone oxime, which may also be helpful to understand the co-catalytic function of ZnCl₂ herein.

Table 2 lists the reaction results of Beckmann rearrangement of cyclohexanone oxime in various solvents, plus the polar property and dielectric constant of the solvents. As seen, MeCN was found to be the most suitable solvent due to the highest conversion and selectivity (entry



Fig. 3 Effect of amount of cocatalyst $ZnCl_2$ on Beckmann rearrangement of cyclohexanone oxime

one). The fact that MeCN tends to exhibit a better result in Beckmann rearrangement has been observed by other researchers [7, 8, 17]. The previous study [7] has revealed that a polar solvent is more favourable to this reaction. As an aprotic polar solvent with strong nucleophilicity, MeCN facilitates the reaction mostly by stabilizing the reaction intermediates such as N-protonated oxime [39]. On the other hand, Shiju et al. [20] have found that the solvents with higher dielectric constants may accelerate the 1,2-H shift of N-protonated oxime into O-protonated oxime by reducing the energy barrier of the transition state. This proposal also explains the much better reaction result in MeCN solvent with the highest dielectric constant.

However, in Table 2, another aprotic polar solvent DMF (entry two) gave a low conversion, though it has a very high dielectric constant. This phenomenon is suggested to associate with its unnegligible basicity that should somewhat neutralize the acidic catalyst and therefore hinder the catalytic activity [16, 40]. Moreover, it is understandable that 1,4-dioxane and toluene presented low conversions (entries three and four), considering their extremely low dielectric constants. In addition, toluene actually made the catalyst inactive, which relates to its nonpolar property, causing a mass transfer problem in the resulting liquidliquid-solid triphasic system. On the other hand, the protic solvents like ethanol with a moderate dielectric constant is not a suitable solvent for this reaction, as also reported previously [39] despite its polar nature. It is true that ethanol only led to a low activity over the present [MIMPS]₃PW₁₂O₄₀ catalyst (entry five). Ethanol has a weaker nucleophilicity than MeCN, which may be the major reason for its low conversion.

Table 2 Influence of solvents on Beckmann rearrangement of cyclohexanone oxime catalyzed by $[MIMPS]_3PW_{12}O_{40}$

Entry	Solvent	Polarity ^a	Dielectric constant ^b	Conv./ %	Sel./ %
1	MeCN	Aprotic polar	37.5	100	83
2	DMF	Aprotic polar	36.7	7	71
3	1,4- Dioxane	Aprotic polar	2.2	17	50
4	Toluene	Nonpolar	2.0	0	-
5	EtOH	Protic polar	24.5	10	83

Cyclohexanone oxime 2 mmol, catalyst 0.2 mmol, ZnCl_2 0.6 mmol, solvent 5 mL, 90 °C, 1 h

^a Referring to Philip G. Jessop (2011) Green Chem 13:1391

^b Referring to Ronchin L, Vavasori A, Bortoluzzi M (2008) Catal Commun 10:251 3.3 Recycling of Catalyst [MIMPS]₃PW₁₂O₄₀ for Beckmann Rearrangement of Cyclohexanone Oxime

Since $[MIMPS]_3PW_{12}O_{40}$ is a solid heterogeneous catalyst for Beckmann rearrangement of cyclohexanone oxime, it can be easily recovered from a reacted mixture. However, ZnCl₂ is partially dissolved in acetonitrile and is totally washed away during a recovery operation. Therefore, catalytic reusability of $[MIMPS]_3PW_{12}O_{40}$ was tested with adding fresh ZnCl₂ in recycling intervals, as shown in Fig. 4. It can be seen that, compared to the fresh catalyst, a substantial decrease in conversion was observed in the second and third runs. However, the conversion was stable in after runs, showing a considerable value above 53 %. Additionally, whatever the recycling numbers, very steady selectivity was found.

Figure 5 illustrates the IR results for [MIMPS]₃ $PW_{12}O_4$. Similar to the fresh catalyst, the recycled one showed four featured bands for Keggin phosphotungstateanion at 1,079, 979, 896, and 806 cm⁻¹ [24]. For the cation moiety MIMPS, the bands at 1,230, 1,172, and 621 cm^{-1} appeared for the sulfonic group, with simultaneous occurrence of 1,617 cm^{-1} for the vibration of C=C and 1,638 cm⁻¹ for C=N. The IR comparison suggests a quite durable structure of [MIMPS]₃PW₁₂O₄₀ in this Beckmann reaction. However, the characteristic vibrations for the product molecule ε -caprolactam (3,412 cm⁻¹ for N-H and 1,400 cm⁻¹ for C-N) also appeared on the recycled [MIMPS]₃PW₁₂O₄₀. It is thus deduced that the contamination of the active acidic sites by the involved basic *ɛ*-caprolactam molecules may account for the decreases of conversion in the early two recycling runs.

Such an interpretation was also revealed by Du's work [40]. Additionally, the contamination of the catalyst acidic sites by the residue of the basic substrate cyclohexanone oxime cannot be excluded, because of the largely enhanced band at $1,638 \text{ cm}^{-1}$ for C=N on the recycled catalyst. To improve the recycling stability of the present catalytic system remains a further work.

3.4 Beckmann Rearrangement of Various Ketoxime Substrates Catalyzed by [MIMPS]₃PW₁₂O₄₀–ZnCl₂

To explore the scope of Beckmann rearrangement catalyzed by [MIMPS]₃PW₁₂O₄₀ and ZnCl₂, various ketoximes substrates were examined. As indicated in Table 3, higher yields 88-98 % were obtained for aromatic ketoximes (entries 1-4) than the yield 83 % for cyclohexanone oxime (entry five). Compared to previous results over the catalysts of caprolactam-based Brønsted acidic IL [16], binucleate-SO₃H functionalized imidazolium IL [17], cyclopropenium ion, [6] and cyanuric chloride [7], the present catalyst [MIMPS]₃PW₁₂O₄₀ offers a comparative yield with aromatic ketoximes and a higher yield with alkyl ketoximes, even under milder conditions. In addition, our catalyst gave meliorative yields with the inert substrates cyclopentanone oxime (19%) and acetone oxime (8%) (entries six and seven), and increasing the reaction time up to 6 h resulted in higher yields (74 and 18 %), which is in contrast to the fact that the early effort could not convert the two inert substrates [17]. This again evidences the high catalytic activity of [MIMPS]₃PW₁₂O₄₀ for Beckmann reactions.



Fig. 4 Catalytic recycling of $[MIMPS]_3PW_{12}O_{40}$ for Beckmann rearrangement of cyclohexanone oxime



Fig. 5 IR spectra of (a) fresh [MIMPS] $_3PW_{12}O_{40}$ and (b) recycled [MIMPS] $_3PW_{12}O_{40}$ after five runs

Table 3Beckmannrearrangements of varioussubstrates catalyzed by[MIMPS]_3PW_{12}O_{40}-ZnCl_2

Entry	Oxime substrate	Amide product	Yield /% ^a
1	N ^{OH} Ph ^{Ph} Ph	Ph N ^{-Ph} H	98
2	N ^{OH} H	O N-Ph H	88
3	MeO	MeO	88
4	N ^{OH}	O ₂ N H	95
5	N ^{,OH}	O NH	83
6	N OH	O NH	19 (74 ^b)
7	N OH	O N H	8 (18 ^b)

Reaction conditions: Oxime 2 mmol, $[MIMPS]_3PW_{12}O_{40}$ 0.2 mmol, $ZnCl_2$ 0.6 mmol, MeCN 5 ml, 90°C, 1 h ^a GC yield ^b 6 h

4 Conclusions

The heteropolyanion-based IL [MIMPS]₃PW₁₂O₄₀ containing propane sulfoacid-functionalized imidazolium cation and Keggin phosphotungstate anion is revealed to be highly efficient catalyst for Beckmann rearrangement with ZnCl₂ as the cocatalyst. Ten mol percentage IL catalyst with 30 mol % ZnCl₂ well converts cyclohexanone oxime or aromatic oximes to corresponding amides within 1 h at 90 °C. With a longer reaction time 6 h, the catalyst is even active for the inert substrates cyclopentanone oxime and acetone oxime. As a solid heterogeneous catalyst, [MIMPS]₃ PW₁₂O₄₀ can be easily recovered after reaction, showing a considerably high activity after five recycling runs of the rearrangement of cyclohexanone oxime.

Acknowledgments The authors thank greatly the National Natural Science Foundation of China (No. 21136005).

References

- 1. Blatt AH (1933) Chem Rev 12:215
- 2. Luedeke VD (1978) In: Mcketta JJ (ed) Encyclopedia of chemical processing and design. Marcel Dekker, New York
- Smith MB, March J (2001) Advanced organic chemistry, 5th edn. Wiley, New York

- 4. Ko Y, Kim MH, Kim SJ, Seo G, Kim MY, Uh YS (2000) Chem Commun 829
- Turgis R, Estager J, Draye M, Ragaini V, Bonrath W, Leveque JM (2010) ChemSusChem 3:1403
- 6. Srivastava VP, Patel R, Yadav G, Yadav LDS (2010) Chem Commun 46:5808
- 7. Furuya Y, Ishihara K, Yamamoto H (2005) J Am Chem Soc 127:11240
- 8. Vilas M, Tojo E (2010) Tetrahedron Lett 51:4125
- 9. Peng J, Deng Y (2001) Tetrahedron Lett 42:403
- Boero M, Ikeshoji T, Liew CC, Terakura K, Parrinello M (2004) J Am Chem Soc 126:6280
- 11. Ikushima Y, Hatakeda K, Sato O, Yokoyama T (2000) J Am Chem Soc 122:1908
- 12. Song HY, Li Z, Chen J (2012) Catal Lett 142:81
- 13. Zhao D, Wu M, Kou Y, Min E (2002) Catal Today 74:157
- 14. Dupont J, Souza RF, Suarez PAZ (2002) Chem Rev 102:3667
- 15. Zicmanis A, Katkevica S, Mekss P (2009) Catal Commun 10:614
- Guo S, Du Z, Zhang S, Li D, Li Z, Deng Y (2006) Green Chem 8:296
- 17. Liu X, Xiao L, Wu H, Li Z, Chen J, Xia C (2009) Catal Commun 10:424
- 18. Qiao Y, Hou Z (2009) Curr Org Chem 13:1347
- Maheswari R, Shanthi K, Sivakumar T, Sankarasubbier N (2003) Appl Catal A 248:291
- 20. Shiju NR, Williams HM, Brown DR (2009) Appl Catal B 90:451
- Bourlinos AB, Raman K, Herrera R, Zhang Q, Archer LA, Giannelis EP (2004) J Am Chem Soc 126:15358
- 22. Ge HQ, Leng Y, Zhou CJ, Wang J (2008) Catal Lett 124:324
- 23. Chaturvedi D (2011) Curr Org Chem 13:1347
- 24. Leng Y, Wang J, Zhu D, Ren X, Ge H, Shen L (2009) Angew Chem Int Ed 48:168

- 25. Leng Y, Wang J, Zhu D, Wu Y, Zhao P (2009) J Mol Catal A 313:1
- 26. Zhang W, Leng Y, Zhu D, Wu Y, Wang J (2009) Catal Commun 11:151
- 27. Zhang W, Leng Y, Zhao P, Wang J, Zhu D, Huang J (2011) Green Chem 13:832
- Leng Y, Wang J, Zhu D, Zhang M, Zhao P, Long ZH, Huang J (2011) Green Chem 13:1636
- 29. Leng Y, Wang J, Zhu D, Shen L, Zhao P, Zhang M (2011) Chem Eng J 173:620
- 30. Zhao P, Leng Y, Zhang M, Wang J, Wu Y, Huang J (2012) Chem Commun 48:5721
- 31. Pi HJ, Dong JD, An N, Du W, Deng WP (2009) Tetrahedron 65:7790

- 32. Dupont J, Spencer J (2004) Angew Chem Int Ed 43:5296
- 33. Cheng SB, Xu BQ, Wang DQ (1996) Chin J Catal 17:281
- Hill RK, Conley RT, Chortyk OT (1965) J Am Chem Soc 87:24
 Ronchin L, Bortoluzzi M, Vavasori A (2008) J Mol Theochem
- 858:46 36. Nguyen MT, Raspoet G, Vanquickenborne LG (1997) J Am Chem Soc 119:2552
- 37. Zhang X, Li J, Wang XH, Cao FH (2009) Energy Fuels 23:4640
- Ronchin L, Vavasori A, Bortoluzzi M (2008) Catal Commun 10:251
- 39. Wang XG, Chen CC, Chen X, Mou Y, Cheng S (2005) Appl Catal A 281:47
- 40. Du Zh, Li Z, Gu Y, Zhang J, Deng Y (2005) J Mol Catal A 237:80