RSC Advances

PAPER

Cite this: RSC Adv., 2014, 4, 6159

Received 13th November 2013 Accepted 13th December 2013

DOI: 10.1039/c3ra46559d

www.rsc.org/advances

Introduction

Solid superbases are materials that possess basic sites with strength (H_{-}) higher than 26 (H_{-} corresponding to the pK_a value of the indicator).¹ The use of solid superbases has attracted much attention because they catalyze a number of organic reactions under mild conditions, resulting in a significant reduction in pollutant generation.¹⁻³ In the past decades, there were reports on solid superbase catalysts such as KNO₃/ γ -Al₂O₃,^{4,5} KNO₃/ZrO₂,^{6,7} KF/ γ -Al₂O₃,⁸ KOH/ZrO₂,⁹ K₂CO₃/ γ -Al₂O₃ ¹⁰ and Ca(NO₃)₂/SBA-15.¹¹ It is noted that only a few types of materials were employed as supports for the preparation of superbases, *viz.* γ -Al₂O₃,^{4,5,8} ZrO₂ ^{6,7,9} and SBA-15 mesoporous molecular sieve.¹¹ Therefore, the selection and/or synthesis of suitable materials as supports for the synthesis of superbases should be considered essential for future development of superbases.

In recent years, MgO–ZrO₂ has been widely used as solid catalysts or basic supports in various chemical reactions (*e.g. O-tert*-Boc protection of alcohols and phenols,¹² alkylation,¹³ aldol condensation,^{14–17} Knoevenagel condensation¹⁸ and transesterification^{19–21}). However, there is no report on magnesium–zirconium composite oxides with sites that are superbasic. In a study of Clacens *et al.*, it was observed that the use of

Novel and versatile solid superbases derived from magnesium-zirconium composite oxide and their catalytic applications

Jin Zhao,^a Jun Xie,^a Chak-Tong Au^{ab} and Shuang-Feng Yin*^a

Versatile solid superbases were derived from magnesium-zirconium composite oxide and KOH through thermal treatment in a N₂ flow. The magnesium-zirconium composite oxide was prepared by a modified co-precipitation technique with reflux-digestion in basic solution and then mixed with KOH through grinding. The as-prepared solid superbases were characterized by low-temperature N₂ physisorption, powder X-ray diffraction, and Fourier transformation infrared spectrophotometry. The superbasic sites were characterized by the use of Hammett indicators and CO₂ temperature-programmed desorption methods. We found that there are ample superbasic sites (0.590 mmol g⁻¹) on the surface with strength in the 26.5 \leq H₋ < 33.0 range. The as-prepared solid superbase catalyst was found to show excellent catalytic activity towards Knoevenagel condensation, Michael addition and transesterification reactions. The findings open up a new route for the synthesis of new functional superbases using composite oxides prepared by reflux-digestion in basic solution as supports.

> a basic support could result in the generation of stronger basic sites.²² Previously, we synthesized a KOH/La₂O₃–MgO solid superbase catalyst by co-precipitation.²³ In the present work, we prepared MgO–ZrO₂ support large (165.9 m² g⁻¹) in surface area by reflux-digestion in a basic solution. We describe herein the synthesis of a series of solid superbases using the magnesium– zirconium composite oxide as support and KOH as modifier. We characterized the structure and surface properties of the KOH/MgO–ZrO₂ samples. The as-prepared solid superbase were tested as catalysts for a number of important organic basecatalyzed reactions, *viz.* Knoevenagel condensation, Michael addition and transesterification.

Results and discussion

Displayed in Fig. 1 are the XRD patterns of MgO–ZrO₂ and KOH/ MgO–ZrO₂ samples. We detect MgO and magnesium–zirconium composite oxide (Mg₂Zr₅O₁₂ JCPDS file 80-967) but not ZrO₂ in the MgO–ZrO₂ sample (Fig. 1a). It is induced that the octahedral vacant sites on the surface of ZrO₂ prompt the Mg²⁺ ions to occupy the position of octa-coordinated Zr⁴⁺, leading to the strong interaction of MgO with ZrO₂,²¹ consequently facilitating the formation of superbase sites. Similar phenomenon was also observed in previous reports.^{6,7} With the loading of 7 or 14 wt% of KOH on MgO–ZrO₂ (Fig. 1b and c), the obtained patterns are similar to that of MgO–ZrO₂. Nonetheless extremely weak signals of KOH are observed when KOH loading is 21 wt% (JCPDS file 21-645) (Fig. 1d), and these signals become evident at KOH loading of 28 wt% (Fig. 1e). It is clear that there exists a dispersion threshold of KOH on MgO–ZrO₂, a kind similar to



View Article Online

View Journal | View Issue

^aState Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, Hunan, China. E-mail: sf_yin@hnu.edu.cn; Fax: +86-731-88821171; Tel: +86-731-88821171 ^bDepartment of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China



Fig. 1 XRD patterns of (a) MgO–ZrO₂ (b) 7% KOH/MgO–ZrO₂ (c) 14% KOH/MgO–ZrO₂ (d) 21% KOH/MgO–ZrO₂ (e) 28% KOH/MgO–ZrO₂. *: Mg₂Zr₅O₁₂, ◆: MgO, •: KOH.



The BET surface area and pore volume of MgO–ZrO₂ and KOH/MgO–ZrO₂ catalysts of different KOH loadings are given in Table 1. The BET surface area of MgO–ZrO₂ is 165.9 m² g⁻¹. With increase of KOH content, there is decrease of specific surface area as well as pore volume. The results suggest that there is the diffusion of potassium species into the pores of MgO–ZrO₂.

Fig. 2 gives the IR spectra of as-synthesized MgO–ZrO₂ and 21 wt% KOH/MgO–ZrO₂. For the two samples, the broad band at around 3450 cm⁻¹ is assigned to OH stretching vibration of the hydroxyl groups attached to Mg. The bands in the 400–700 cm⁻¹ region are ascribable to the vibration of ZrO₂²⁴ whereas those in the 1300–1450 cm⁻¹ region are attributable to the vibration of CO_3^{2-} , with the latter being stronger than the former.^{25–27} The results demonstrate that with the introduction of KOH, there is the creation of basic sites and promotion of CO₂ adsorption.

The base strength (H_{-}) and amount of basic sites of samples were measured using Hammett indicators (Table 1). One can see that the basic strength of MgO–ZrO₂ is in the 15.0 $\leq H_{-} <$ 18.4 range. With the introduction of KOH, basic strength of KOH/MgO–ZrO₂ samples are in the 26.5 $\leq H_{-} <$ 33.0 range. It is clear that the KOH/MgO–ZrO₂ materials can be regarded as solid superbases.¹ The KOH/MgO–ZrO₂ samples are different in the amount of superbasic sites, showing a maximum (0.59 mmol g⁻¹) at KOH loading of 21%. In other words, to

Table 1 Physicochemical characteristics of $\text{MgO}-\text{ZrO}_2$ and KOH/ $\text{MgO}-\text{ZrO}_2$ samples

KOH loading (wt%)	${S_{\mathrm{BET}}}^a$ $\left(\mathrm{m}^2~\mathrm{g}^{-1} ight)$	$V_{ ho}^{\ b}$ (cm ³ g ⁻¹)	Base strength (<i>H</i> _)	Superbasic sites (mmol g^{-1})
0	165.9	0.536	$15.0 \le H_{-} < 18.4$	0
7	139.5	0.454	$26.5 \le H_{-} < 33.0$	0.297^c , 0.284^d
14	91.1	0.361	$26.5 \le H_{-} < 33.0$	$0.468^c, 0.446^d$
21	50.7	0.240	$26.5 \le H_{-} < 33.0$	$0.590^c, 0.553^d$
28	34.6	0.163	$26.5 \leq H < 33.0$	0.361 ^c , 0.318 ^d

 a $S_{\rm BET}$: BET specific surface area. b V_ρ : pore volume. c Measured by Hammett indicators method. d Measured by CO₂-TPD.



Fig. 2 FT-IR spectra of (a) MgO-ZrO₂ and (b) 21% KOH/MgO-ZrO₂.

optimize the generation of superbasic sites, potassium loading around 21% is the most appropriate, consistent with the results of XRD investigation.

The basicity of samples was further investigated by CO_2 -TPD. As depicted in Fig. 3, the MgO-ZrO₂ sample shows main desorption peaks at ca. 143 and 568 °C. After the introduction of KOH, desorption peaks are observed at ca. 144, 286, 588 and 653 °C. The emergence of desorption peaks at *ca.* 653 °C is a clear indication of superbasicity.27,29 The amounts of superbasic sites on the 7, 14, 21, 28 wt% KOH/MgO-ZrO₂ samples as calculated by the integral method based on the area of the corresponding desorption peaks are 0.284, 0.446, 0.553 and 0.318 mmol g^{-1} respectively (Table 1). According to the reports of Zhu and co-workers, there exits an overlapping structure of basic species formed on their samples.^{4,7} With such an overlapping structure, basic species covered by the upper layers were not exposed to CO₂, but would react with an acidic agent if the top layers were dissolved in an aqueous titration process. As a result, the CO₂-TPD data only reveal the amount of basic sites exposed at the top of the overlapped structure while the titration data represent the total basicity of the composite, with the former smaller than the latter. It is hence considered that the CO₂-TPD results are in good agreement with those obtained by the Hammettindicator method (Table 1).

The Knoevenagel condensation reaction is important for the formation of C=C double bond between carbonyl and active



Fig. 3 CO2-TPD profiles of (a) MgO–ZrO2 and (b) 21% KOH/MgO–ZrO2.

methylene compounds.^{18,28–30} Depicted in Table 2 are the results of Knoevenagel condensation of various aldehydes with active methylene compounds over 21 wt% KOH/MgO–ZrO₂. In all cases the products are generated in good to excellent yield, comparable or superior to those of solid bases such as $Ce_xZr_{1-x}O_2$, In/AlMCM-41, MgO–ZrO₂ and LDH-F.^{18,29–31} Namely, the 21 wt% KOH/MgO–ZrO₂ catalyst can be regarded as an excellent catalyst for Knoevenagel condensation reactions.

Michael addition is widely used for C–C bond formation in organic synthesis.^{30–34} We report here the catalytic properties of 21 wt% KOH/MgO–ZrO₂ for different Michael additions (Table 3). A comparison of substrates with different pK_a not only allows us to estimate the reactivity of the catalyst but also enable us to evaluate the basic strength of the catalyst surface.³⁵ The fast reactions at RT demonstrate that 21 wt% KOH/MgO–ZrO₂ has sites of high basic strength able to abstract a proton from reactants of high pK_a . The high yield and short reaction time at RT and atmospheric pressure confirm that the strong basic sites on 21 wt% KOH/MgO–ZrO $_2$ are suitable for this kind of base-catalyzed processes.

Transesterification of ester with alcohol is important in the synthesis of fine chemicals, and is commonly catalyzed by basic materials.^{26,36,37} We used 21 wt% KOH/MgO-ZrO₂ to catalyze the transesterification of propylene carbonate (PC) with methanol to produce DMC and propylene glycol (PG). The results are shown in Fig. 4. It is worth noting that the yield of DMC reaches 53.3% at a reaction time of 1 h and increases to 68.2% at 3 h under atmospheric pressure, higher than those recorded in the literatures.^{26,36,37} It is observed that the DMC yield remains almost constant even the reaction is prolonged to 5 h, suggesting that the reaction is limited by thermodynamic equilibrium.³⁸ For comparison, the typical solid base MgO-ZrO2 and MgO were employed to catalyze the transesterification reaction. Under the same reaction conditions, only 12.7% and 10.4% of DMC was produced at 3 h respectively. This demonstrates the excellent catalytic performance of the 21 wt% KOH/MgO-ZrO2 catalyst.

Entry	R	R^1	Catalyst	Time/min	Yield (%)	Ref.
1	C_6H_5	CN	21 wt% KOH/MgO–ZrO ₂	15	98.2	
			$Ce_x Zr_{1-x}O_2$	50^b	82^b	28
			MgO-ZrO ₂	20^{c}	93 ^c	17
			In/AlMCM-41	25^d	95^d	29
2	C_6H_5	COOEt	21 wt% KOH/MgO–ZrO ₂	60	96.2	
			$Ce_xZr_{1-x}O_2$	75^b	78^b	28
			LDH-F	120^{e}	92^{f}	30
			MgO-ZrO ₂	90 ^c	80 ^c	17
3	$4-NO_2C_6H_4$	CN	21 wt% KOH/MgO-ZrO ₂	15	97	
			$Ce_xZr_{1-x}O_2$	45^b	90^b	28
			MgO-ZrO ₂	20^{c}	67 ^c	17
			In/AlMCM-41	45^d	89^d	29
4	$4-NO_2C_6H_4$	COOEt	21 wt% KOH/MgO-ZrO ₂	60	98.7	
			$Ce_rZr_{1-r}O_2$	55^{b}	85^b	28
			MgO-ZrO ₂	90 ^c	88 ^c	17
			In/AlMCM-41	150^d	79^d	29
5	$4-ClC_6H_4$	CN	21 wt% KOH/MgO-ZrO ₂	15	93.6	
			$Ce_x Zr_{1-x}O_2$	60^b	81^b	28
			MgO-ZrO ₂	20^{c}	65 ^c	17
6	$4-ClC_6H_4$	COOEt	21 wt% KOH/MgO-ZrO ₂	60	94.3	
			$Ce_x Zr_{1-x}O_2$	60^b	78^b	28
			LDH-F	120^{e}	86 ^f	30
			MgO-ZrO ₂	90 ^c	65 ^c	17
7	$4-CH_3C_6H_4$	CN	21 wt% KOH/MgO-ZrO ₂	15	97.8	
			$Ce_xZr_{1-x}O_2$	60^b	78^b	28
			MgO-ZrO ₂	20^{c}	82 ^c	17
			In/AlMCM-41	30^d	91^d	29
8	$4-CH_3C_6H_4$	COOEt	21 wt% KOH/MgO–ZrO ₂	60	91.9	
			$Ce_xZr_{1-x}O_2$	90^b	72^b	28
			MgO-ZrO ₂	90 ^c	84 ^c	17
			In/AlMCM-41	110^d	82^d	29
9	$4-CH_3OC_6H_4$	CN	21 wt% KOH/MgO–ZrO ₂	15	91.4	
			MgO-ZrO ₂	20^{c}	68 ^c	17
			In/AlMCM-41	40^d	88^d	29
10	$4-CH_3OC_6H_4$	COOEt	21 wt% KOH/MgO-ZrO ₂	60	87	
			In/AlMCM-41	145^d	78^d	29

^{*a*} *Reaction conditions*: aldehyde (2 mmol), active methylene compound (2 mmol), catalyst (0.035 g), DMF (1 ml), RT. ^{*b*} Aldehyde (1 mmol), active methylene compound (1.1 mmol), catalyst (10 wt%), ethanol, 80 °C. ^{*c*} Aldehyde (10 mmol), active methylene reagents (10 mmol), catalyst (20 wt%), 60 °C. ^{*d*} Aldehyde (10 mmol), active methylene compound (12 mmol), catalyst (0.1 g), ethanol refluxed. ^{*e*} Aldehyde (1 mmol), active methylene reagents (1.1 mmol), catalyst (0.035 g), DMF (5 ml). ^{*f*} Aldehyde (1 mmol), active methylene reagents (1.1 mmol), catalyst (0.035 g), DMF or MeCN (5 ml).

Table 3	Michael addition results over	21 wt% KOH/MgO-Z	rO ₂ and some other c	atalysts reported in	the literature
		<u> </u>		2 1	

Entry	Donor	pK_a in DMSO	Catalyst	Reaction time (h)	Yield (%)	Ref.
	,CN		21 wt% KOH/MgO-ZrO ₂	0.15	99.2	
	$\leq_{\rm CN}$		Modified Mg–Al hydrotalcite	2^b	88^b	31
1	CN	11.1	MgO	1.5^{c}	88 ^c	32
			Mg-La	0.16^{d}	99^d	34
	.CN		21 wt% KOH/MgO-ZrO ₂	0.5	91.7	
2		13.1	MgO	0.5^{c}	88 ^c	32
	CODEt		Mg-La	1.5^d	97^d	31
	COCH3		21 wt% KOH/MgO-ZrO ₂	1	93	
3		14.2	Mg-Al-O-t-Bu	0.16^{e}	86 ^e	33
	COOEt		Mg-La	1^d	82^d	34
			21 wt% KOH/MgO-ZrO ₂	1	94.8	
	COOEt		Mg-Al-O-t-Bu	2^e	95^e	33
4	COOEt	16.4	Modified Mg-Al hydrotalcite	6^b	96^b	31
			MgO	2^{c}	93 ^c	32
			LDH-F	2^{f}	95^{f}	30
	.COOCH ₂		21 wt% KOH/MgO-ZrO ₂	1	95.2	
5	$<_{\rm COOCH_3}$	16.4	Mg–Al– <i>O-t</i> -Bu	1 ^e	92 ^e	33
6	CH ₃ NO ₂	17.2	21 wt% KOH/MgO-ZrO ₂	0.5	97.4	
			Mg-Al-O-t-Bu	0.16^{e}	93 ^e	33
			Mg-La	2^d	98^d	34
			LDH-F	2^{f}	90 ^f	30

^{*a*} Reaction conditions: acceptor (1 mmol), donor (1.1 mmol), catalyst (0.05 g), DMF (2 ml). ^{*b*} Acceptor (2 mmol), donor (2 mmol), catalyst (0.2 g), methanol (10 ml). ^{*c*} Acceptor (2 mmol), donor (2 mmol), catalyst (0.05 g), DMF (2 ml). ^{*d*} Acceptor (2 mmol), donor (2.2 mmol), catalyst (0.1 g), DMF (4 ml). ^{*e*} Acceptor (2 mmol), donor (2 mmol), catalyst (0.1 g), methanol (10 ml). ^{*f*} Acceptor (1 mmol), donor (1 mmol), catalyst (0.1 g), MeCN (5 ml).



Fig. 4 DMC yield vs. time in the transesterification of PC with methanol over 21% KOH/MgO-ZrO₂.

We also tested the recyclability of the catalyst for the transesterification of propylene carbonate (PC) with methanol (Fig. 5). After each run, the catalyst was separated from the product by centrifugation, and was immediately reused (with the addition of fresh reactants) without any treatment. We observed that there is an obvious decrease of product yield across the five runs. The deactivation of catalyst is likely due to the blocking of basic and superbasic sites by organic entities. We find that once the organic entities are removed through the adopted calcination process, the spent catalyst recovers in activity (see number 6 and 7 in Fig. 5). Therefore, the superbase catalyst is highly recyclable and reusable.



Fig. 5 Recyclability profile of 21% KOH/MgO– ZrO_2 in transesterification reaction.

Experimental

Catalysts preparation

Magnesium–zirconium composite oxide (Mg/Zr molar ratio = 2) was prepared by co-precipitation method. Required amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 5H_2O$ were dissolved in distilled water separately to form transparent solutions, which were then mixed together. 1 M KOH aqueous solution was added dropwise to the mixture under stirring until a pH of 10–12. The mixture was digested under reflux at 366 K for 24 h, and then subject to filtration and washing with water until the pH value of filtrate was near 7. The as-obtained solid substance was

dried at 383 K overnight and calcined at 823 K for 4 h to get magnesium-zirconium composite oxide.

The KOH-modified MgO– ZrO_2 samples were prepared by grinding method, followed by thermal treatment under a flow of N₂ (purity: 99.999%) at 500 °C for 2 h. The as-prepared sample is denoted hereinafter as "*x* wt% KOH/MgO– ZrO_2 ", where *x* stands for the weight percentage of KOH in terms of the whole catalyst.

Catalyst characterization

XRD patterns were recorded on a Brucker D8 advance diffractometer with monochromatized Cu K α radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 40 mA. The specific surface areas of catalysts were determined by BET method based on nitrogen adsorption-desorption isotherms (at 77 K) collected over a Beckman (SA 3100) surface area analyzer. The FTIR spectra were determined using a Bruker vector 22 FTIR spectrophotometer (using KBr tablets). CO2-TPD measurements were conducted on a Micromeritics 2920 apparatus using thermal conductivity detector. The sample was activated at 400 °C for 2 h prior to the adsorption of CO₂ at 100 °C. After purging the physically adsorbed CO_2 at 100 °C, the sample was heated to 850 °C at a rate of 8 °C \min^{-1} . The base strength (H_{-}) of the sample was also determined by Hammett indicators.³⁹ To measure the total basicity, the activated samples was immersed in 0.05 mol l⁻¹ HCl (20 ml) with stirring, and the remaining acid was then titrated against standard NaOH solution (0.02 mol l^{-1}).

Catalyst evaluation

Knoevenagel condensation of aldehydes and methylene compounds was performed at RT in a glass reactor (Scheme 1). In a typical run, aldehyde (2 mmol), active methylene reagent (2 mmol), catalyst (20 mg), and DMF (1 ml) were mixed in a 25 ml round-bottomed flask. The reaction was monitored by thin layer chromatography (TLC). After the reaction, the mixture was subject to centrifugation for catalyst recovery. The reaction mixtures were analyzed using an Agilent Technologies 7820 gas chromatograph equipped with a flame ionization detector (FID) and AB-FFAP capillary column (30 m \times 0.25 mm \times 0.25 μ m). The conversion of aldehyde was determined using biphenyl as internal standard.

Michael addition of chalcone and methylene compounds was performed in a glass reactor (Scheme 2). Chalcone (1 mmol), methylene compounds (1 mmol), catalyst (0.05 g) and DMF (2 ml) were added and the mixture was stirred at RT for an appropriate period of time. After reaction completion (monitored by TLC), the mixture was subject to centrifugation for catalyst recovery. The reaction mixture was analyzed using an



R-H,NO₂,Cl,CH₃,OCH₃;R₁-COOEt,CN





Scheme 2 Michael addition of chalcone and methylene compounds.

$$\bigcup_{O} = O + CH_3OH \xrightarrow{Cat.} O + OH \xrightarrow{O} OH$$

Scheme 3 Transesterification of cyclic carbonate with methanol to produce DMC.

Agilent Technologies 7820 GC equipped with a FID and HP-5 capillary column (30 m \times 0.32 mm \times 0.25 μm). The conversion of chalcone was determined using biphenyl as internal standard.

Transesterification of propylene carbonate with methanol to produce dimethyl carbonate (DMC) was carried out at 353 K using 0.01 mol propylene carbonate, 0.10 mol of methanol, and 100 mg catalyst in a glass batch reactor equipped with condenser and a magnetic stirrer (Scheme 3). The analysis of products was similar to that of Michael addition.

Conclusions

A versatile solid superbase material has been obtained by loading KOH onto magnesium–zirconium composite oxide of high surface area, followed by thermal treatment at 500 °C under a flow of high-purity N₂. There are ample superbasic sites up to 0.590 mmol g⁻¹ with strength in the 26.5 $\leq H_{-} < 33.0$ range. The materials show high catalytic activity and selectivity in Knoevenagel condensation, Michael addition and transesterification reactions. The one with 21 wt% KOH loading is the best, showing the highest superbasicity and catalytic activity. It is envisaged that this versatile catalyst is also useful for other important organic reactions and has a wide scope in catalysis technology.

Acknowledgements

The project was financially supported by the National Natural Science Foundation of China (Grant no. U1162109), the program for New Century Excellent Talents in Universities (NCET-10-0371), Program for Changjiang Scholars and Innovative Research Team in University (IRT1238), and the Fundamental Research Funds for the Central Universities. C. T. Au thanks the Hunan University for an adjunct professorship.

Notes and references

1 K. Tanabe, M. Misono, Y. Ono and H. Hattori, *New Solid Acids and Bases, Their Catalytic Properties*, Kodansha, Tokyo, 1989, p. 3.

- 2 H. Hattori, Chem. Rev., 1995, 95, 537-558.
- 3 Y. D. Wei, S. G. Zhang, G. X. Li, S. Y. Yin and C. T. Au, *Chin. J. Catal.*, 2011, **32**, 891–898.
- 4 J. H. Zhu, Y. Wang, Y. Chun and X. S. Wang, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1163–1169.
- 5 L. B. Sun, J. Yang, J. H. Kou, F. N. Gu, Y. Chun, Y. Wang, J. H. Zhu and Z. G. Zou, *Angew. Chem.*, *Int. Ed.*, 2008, 47, 3418–3421.
- 6 Y. Wang, W. Y. Huang, Z. Wu, Y. Chun and J. H. Zhu, *Mater. Lett.*, 2000, **46**, 198–204.
- 7 Y. Wang, W. Y. Huang, Y. Chun, J. R. Xia and J. H. Zhu, *Chem. Mater.*, 2001, **13**, 670–677.
- 8 H. Tsuji, H. Kabashima, H. Kita and H. Hattori, *React. Kinet. Catal. Lett.*, 1995, **56**, 363–369.
- 9 S. F. Yin, B. Q. Xu, S. J. Wang and C. T. Au, *Appl. Catal., A*, 2006, **301**, 202–210.
- 10 Y. Wang, J. H. Zhu and W. Y. Huang, *Phys. Chem. Chem. Phys.*, 2001, 3, 2537–2543.
- 11 L. B. Sun, J. H. Kou, Y. Chun, J. Yang, F. N. Gu, Y. Wang, J. H. Zhu and Z. G. Zou, *Inorg. Chem.*, 2008, 47, 4199–4208.
- 12 M. B. Gawande, S. N. Shelke, P. S. Branco, A. Rathi and R. K. Pandey, *Appl. Organomet. Chem.*, 2012, 26, 395–400.
- 13 D. Ciuparu, A. Ensuque and F. Bozon-Verduraz, *Appl. Catal.*, *A*, 2007, **326**, 130–142.
- 14 M. B. Gawande, P. S. Branco, K. Parghi, J. J. Shrikhande, R. K. Pandey, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro and R. V. Jayaram, *Catal. Sci. Technol.*, 2011, 1, 1653–1664.
- 15 I. Sádaba, M. Ojeda, R. Mariscal, R. Richards and M. López Granados, *Catal. Today*, 2011, **167**, 77–83.
- 16 W. Q. Shen, G. A. Tompsett, K. D. Hammond, R. Xing, F. Dogan, C. P. Grey, W. Curtis Conner Jr, S. M. Auerbach and G. W. Huber, *Appl. Catal.*, A, 2011, 392, 57–68.
- 17 I. Sádaba, M. Ojeda, R. Mariscal, J. L. G. Fierro and M. López Granados, *Appl. Catal., B*, 2011, **101**, 638–648.
- 18 M. B. Gawande and R. V. Jayaram, *Catal. Commun.*, 2006, 7, 931–935.
- 19 S. G. Liu, X. L. Zhang, J. P. Li, N. Zhao, W. Wei and Y. H. Sun, *Catal. Commun.*, 2008, **9**, 1527–1532.
- 20 R. Sree, N. Babu Seshu, P. S. Sai Prasad and N. Lingaiah, *Fuel Process. Technol.*, 2009, **90**, 152–157.

- 21 Y. S. Li, S. Lian, D. M. Tong, R. L. Song, W. Y. Yang, Y. Fan, R. W. Qing and C. W. Hu, *Appl. Energy*, 2011, 88, 3313–3317.
- 22 J. M. Clacens, D. Genuit, L. Delmotte, A. Garcia-Ruiz,
 G. Bergeret, R. Montiel, J. Lopez and F. Figueras, *J. Catal.*,
 2004, 221, 483–490.
- 23 Y. D. Wei, S. G. Zhang, S. Y. Yin, C. Zhao, S. L. Luo and C. T. Au, *Catal. Commun.*, 2011, **12**, 1333–1338.
- 24 V. Y. Joshi and M. R. Sawant, *Catal. Commun.*, 2007, **8**, 1255–1262.
- 25 S. G. Liu, S. Y. Huang, L. X. Guan, J. P. Li, N. Zhao, W. Wei and Y. H. Sun, *Microporous Mesoporous Mater.*, 2007, **102**, 304–309.
- 26 T. T. Li, L. B. Sun, L. Gong, X. Y. Liu and X. Q. Liu, J. Mol. Catal. A: Chem., 2012, 352, 38-44.
- 27 Y. P. Fan, Q. Y. Wang, X. G. Yang, J. Yao and G. Y. Wang, *Chin. J. Chem. Eng.*, 2009, **17**, 883–886.
- 28 S. G. Zhang, Y. D. Wei, S. F. Yin, S. L. Luo and C. T. Au, *Appl. Catal.*, A, 2011, 406, 113–118.
- 29 G. Postole, B. Chowdhury, B. Karmakar, K. Pinki, J. Banerji and A. Auroux, *J. Catal.*, 2010, **269**, 110–121.
- 30 S. S. Katkar, M. K. Lande, B. R. Arbad and S. B. Rathod, Bull. Korean Chem. Soc., 2010, 31, 1301–1304.
- 31 B. M. Choudary, M. Lakshmi Kantam, V. Neeraja,
 K. Koteswara Rao, F. Figueras and L. Delmotte, *Green Chem.*, 2001, 3, 257–260.
- 32 B. M. Choudary, M. Lakshmi Kantam, Ch. Venkat Reddy, K. Koteswara Rao and F. Figueras, *J. Mol. Catal. A: Chem.*, 1999, **146**, 279–284.
- 33 C. L. Xu, J. K. Bartley, D. I. Enache, D. W. Knight and G. J. Hutchings, *Synthesis*, 2005, 3468–3476.
- 34 B. M. Choudary, M. Lakshmi Kantam, B. Kavita, Ch. Venkat Reddy and F. Figueras, *Tetrahedron*, 2000, 56, 9357–9364.
- 35 V. Bhaskar, J. M. Clacens and F. Figueras, *Adv. Synth. Catal.*, 2005, **347**, 767–771.
- 36 T. Wei, M. H. Wang, W. Wei, Y. H. Sun and B. Zhong, *Fuel Process. Technol.*, 2003, **83**, 175–182.
- 37 P. Unnikrishnan and D. Srinivas, *Ind. Eng. Chem. Res.*, 2012, 51, 6356–6363.
- 38 K. Torii and T. Iwasaki, Catal. Lett., 1986, 2021-2024.
- 39 S. G. Zhang, Y. D. Wei, S. F. Yin and C. T. Au, *Catal. Commun.*, 2011, **12**, 712–716.