

An easy-to-use heterogeneous promoted zirconia catalyst for Knoevenagel condensation in liquid phase under solvent-free conditions

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Abstract

Knoevenagel condensation of various aliphatic, aromatic and heterocyclic aldehydes with malononitrile was carried out in the liquid phase in one step by employing a sulfate-ion promoted zirconia solid acid catalyst. This catalyst facilitates the reaction under solvent-free conditions at moderate temperatures providing excellent yields of the products. The sulfate-ion promoted zirconia catalyst was synthesized by immersing a finely powdered hydrous $Zr(OH)_4$ into the 1 M H_2SO_4 solution and subsequent drying and calcination at 923 K. The $Zr(OH)_4$ was prepared from an aqueous $ZrOCl_2 \cdot 8H_2O$ solution by hydrolysis with dilute aqueous ammonia. The bulk and surface properties of the prepared catalyst was examined by X-ray powder diffraction, BET surface area, temperature programmed desorption of ammonia and Raman spectroscopy techniques. All characterization results revealed that the incorporated sulfate-ions show a significant influence on the surface and bulk properties of the ZrO_2 . In particular, the impregnated sulfate-ions stabilize the metastable zirconia tetragonal phase at ambient conditions and enhance the total number and strength of acid sites.

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1. Introduction

Organic reactions under solvent-free conditions involving easily separable solid catalysts are receiving a considerable attention in recent times, particularly from the viewpoint of green chemistry. As an important carbon–carbon bond forming reaction in organic synthesis, Knoevenagel condensation has been extensively investigated in view of its significance [1]. The Knoevenagel condensation of aldehydes with active methylene compounds has been commonly employed in the synthesis of numerous speciality chemicals and chemical intermediates [1,2] such as carbocyclic as well as heterocyclic compounds of biological significance [3], calcium antagonists [4], polymers [5], coumarin derivatives, cosmetics, perfumes and pharmaceuticals [4,6]. The condensation reaction is generally catalyzed by bases, acids or catalysts containing both acid–base sites [4]. Numerous acid–base reagents or catalysts such as ethylene diamine

[7], dimethyl amino pyridine [8], potassium fluoride mixture [9], surfactants [10], ionic liquids [11], modified silica [12], anionic resins [13], alkaline earth oxides [14], calcined hydro-talcites [15], aluminophosphate oxinitrides [16], alkali cation exchanged X and Y zeolites [17–19] and so on have been reported in the literature. Most of them are used under homogeneous conditions or in the presence of excess solvents, which generate large volumes of waste.

From environment point of view, waste should be eliminated or minimized and obviously bulk wastes in the chemicals manufacturing are often organic solvents. The use of environmentally benign solvents or solvent-free reactions represents an ideal green chemical technology procedure from both economical and environmental point of view. Therefore, efforts have been made to perform the Knoevenagel condensation in the absence of solvents [20,21]. Thus, some approaches could be found in the literature by employing Lewis acids such as SmI_3 [22], $CuCl_2$ [23], $ZnCl_2$ [24], $LaCl_3$ [25], and triphenyl phosphane [26] under solvent-free conditions. It is well known that the use of conventional Lewis acids like $CuCl_2$, $ZnCl_2$ and $LaCl_3$ pose significant risks in handling, containment, disposal and regeneration due to their toxic and corrosive nature. Among the

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solid acid catalysts, sulfate-ion promoted zirconia received much attention recently due to its high thermal stability, large specific surface area, easy recovery and reusability, and ability to perform organic reactions at much lower temperatures [27–32]. Also in recent times, inorganic solid acid catalyzed organic reactions are gaining much attention due to the proven advantage of heterogeneous catalysts such as simplified product isolation, mild reaction conditions, high selectivity, ease in recovery and reuse of the catalysts and reduction in the generation of wasteful products [33–35]. Therefore, the present study was undertaken to exploit the usefulness of the sulfate-ion promoted zirconia solid acid catalyst for Knoevenagel condensation of various aliphatic, aromatic and heterocyclic aldehydes with malononitrile under solvent-free conditions in one step. In this study, a sulfate-ion promoted ZrO_2 and an unpromoted ZrO_2 were synthesized and characterized by BET surface area, X-ray diffraction, NH_3 -TPD and laser Raman spectroscopy techniques, and were evaluated for the title reaction.

2. Experimental

2.1. Catalyst preparation

About 25 g of $ZrOCl_2 \cdot 8H_2O$ (Fluka, GR grade) was dissolved in doubly distilled water. To this clear solution, dilute aqueous ammonia was added drop-wise from a burette with vigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed thoroughly with distilled water until free from chloride ions and dried at 393 K for 16 h. To prepare sulfated ZrO_2 catalyst, a portion of the obtained hydrous zirconia sample was ground to fine powder and immersed in 1 M H_2SO_4 solution (30 ml) for 30 min. Excess water was evaporated on a water-bath and the resulting sample was oven-dried at 393 K for 12 h and calcined at 923 K for 5 h in air atmosphere and stored in a vacuum desiccator. For the purpose of comparison an unpromoted ZrO_2 was also prepared by calcining the hydrous zirconia at 923 K for 5 h in air atmosphere.

2.2. Catalyst characterization

The powder X-ray diffraction patterns have been recorded on a Siemens D-5000 diffractometer by using $Cu K\alpha$ radiation source and a Scintillation counter detector. The XRD phases present in the samples were identified with the help of JCPDS data files. The BET surface area was determined by nitrogen physisorption at liquid nitrogen temperature on a Micromeritics Gemini 2360 instrument. Prior to measurements, samples were oven-dried at 393 K for 10 h and flushed with argon gas for 1 h. Raman spectra were obtained on a DILOR XY spectrometer equipped with a CCD detector. The spectra were recorded using 514.5 nm excitation line from an argon ion laser (Spectra Physics, USA) at a spectral resolution of 2 cm^{-1} . The temperature programmed desorption (TPD) measurements employing NH_3 probe molecule and a thermal conductivity detector were made on an AutoChem 2910 instrument (Micromeritics, USA). Prior to TPD studies, samples were pre-treated at 473 K for 1 h in a flow of ultra pure helium gas (40 ml min^{-1}) and satu-

rated with 10% ultra pure anhydrous ammonia gas (balance He, 60 ml min^{-1}) at 373 K for 2 h and subsequently flushed with He (60 ml min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia.

2.3. Activity studies

All chemicals used in this study were commercially available and used without further purification. In a typical reaction procedure an aldehyde and malononitrile were taken in a 25 ml round bottomed flask fitted with a reflux condenser (1:1.2 mole ratio of aldehyde and malononitrile) and a 0.1 g of catalyst (10 wt.% with respect to the weight of aldehyde) was added. The reaction mixture was stirred in nitrogen atmosphere under solvent-free conditions and heated to reflux conditions. After the completion of the reaction (monitored by TLC), 10 ml of ethyl acetate was added to the reaction mixture and the catalyst was separated by filtration and reused. The excess ethyl acetate was removed by using rotatory-evaporator and the product was chromatographed on a silica gel column to afford the pure products (isolated yields). NMR and mass spectroscopy techniques were used to analyze the products and compared with the authentic samples.

3. Results and discussion

The X-ray powder diffraction patterns of unpromoted and sulfate-ion promoted ZrO_2 samples calcined at 923 K are presented in Fig. 1. As can be noted from this figure, both samples exhibit relatively poor crystallinity with the presence of a mixture of monoclinic and tetragonal phases. Most interestingly, a strong influence on the phase modification from thermodynamically more stable monoclinic to the metastable tetragonal phase is noted when sulfate-ions were incorporated into the $Zr(OH)_4$ structure. The XRD results clearly reveal that the sulfate-ion promoted zirconia exhibits smaller crystallite size and more tetragonal phase (Table 1). It is an established fact in the literature that ZrO_2 -tetragonal phase is more active in catalysis [36]. Generally, incorporation of various promoter atoms such as lanthanum, cerium and yttrium into the zirconia lattice stabilizes the tetragonal phase [37]. The present results are thus inline with earlier observations.

Raman spectra of unpromoted and sulfate-ion promoted zirconia samples calcined at 923 K are shown in Fig. 2. Normally, crystalline ZrO_2 exhibits characteristic Raman bands in the $500\text{--}700\text{ cm}^{-1}$ region. As can be noted from Fig. 2, the spectra of unpromoted ZrO_2 reveal the Raman bands pertaining to a mixture of monoclinic (180, 188, 221, 331, 380, 476 and 637 cm^{-1}) and tetragonal (148, 290, 311, 454 and 647 cm^{-1}) phases and the bands due to tetragonal phase are less intense than the monoclinic phase [38,39]. The spectra of sulfate-ion promoted sample reveals relatively intense Raman bands pertaining to the tetragonal phase. Further, an additional weak band observed at 1032 cm^{-1} could be attributed to the hydrated sulfate groups [40]. Raman results thus support the observations made from XRD studies, wherein sulfate-ion increased the proportion of tetragonal phase.

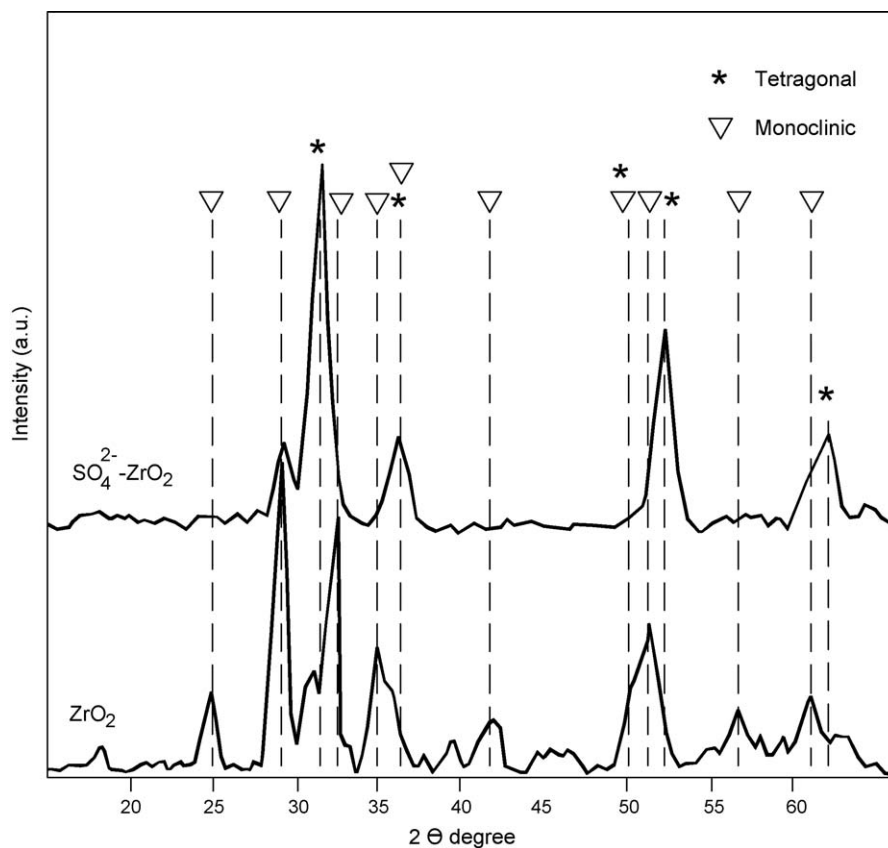


Fig. 1. X-ray powder diffraction patterns of unpromoted and sulfate-ion promoted ZrO_2 samples calcined at 923 K.

Table 1
BET surface area, XRD phases, crystallite size and ammonia desorption amount pertaining to unpromoted and sulfate-ion promoted ZrO_2 samples

Sample	BET SA ($\text{m}^2 \text{g}^{-1}$)	XRD phases				Total NH_3 desorbed (ml g^{-1})
		Monoclinic		Tetragonal		
		Amount (%)	Size (nm)	Amount (%)	Size (nm)	
ZrO_2	42	76	11.2	24	13	5
$\text{SO}_4^{2-}/\text{ZrO}_2$	100	20	7.3	80	12.3	16

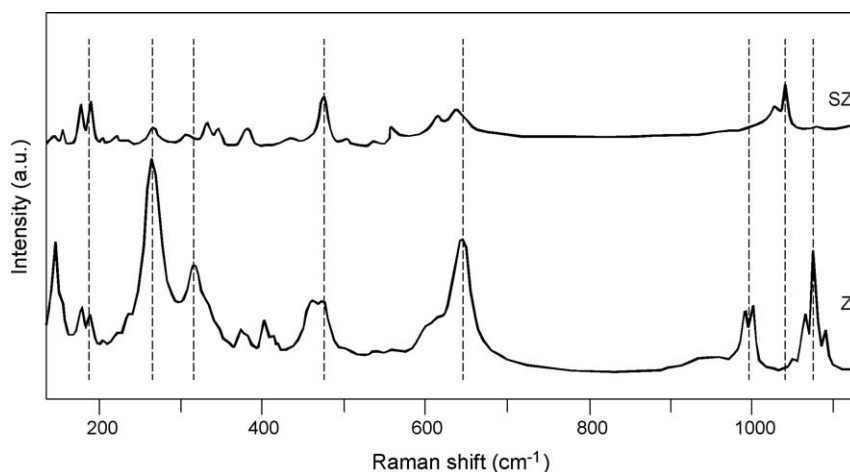
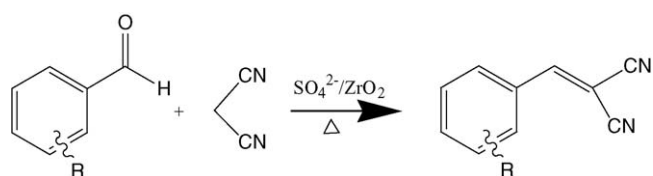


Fig. 2. Raman spectra of unpromoted and sulfate-ion promoted ZrO_2 samples calcined at 923 K.

Table 2

Sulfate-ion promoted ZrO₂ catalyzed Knoevenagel condensation of various aldehydes with malononitrile under solvent-free conditions

S. no.	Aldehyde	Product	Time (min)	Yield (%)
1			180	89
2			30	87
3			45	96
4			150	80
5			45	97
6			35	89
7			120	88
8			150	96
9			35	92
10			45	94
11			45	98
12			300	78
13			300	80

Table 1 represents the BET surface area, amount of NH_3 desorbed, crystallite size and phase composition of unpromoted and sulfate-ion promoted ZrO_2 samples. As can be noted from this table, the sulfate-ion impregnated sample exhibits more specific surface area ($100 \text{ m}^2 \text{ g}^{-1}$) than the unpromoted ZrO_2 ($42 \text{ m}^2 \text{ g}^{-1}$). This is in agreement with previous literature reports where impregnated sulfate-ions were observed to enhance the specific surface area of ZrO_2 [41,42]. The increase in the surface area is due to formation of porous surface sulfate compounds between the impregnated sulfate species and the supporting oxide [42]. As can be noted from Table 1, the sulfated ZrO_2 possesses more tetragonal phase with smaller crystallites (7.3 nm), whereas monoclinic phase with larger crystallites (11.2 nm) is noted in the case of unpromoted sample. As reported in the literature, the final crystal phase and its size mainly depend on the sample history and the calcination temperature employed [43]. Upon thermal treatments, amorphous zirconia is normally transformed into a metastable tetragonal phase. With increasing treatment temperature, crystallization increases and the tetragonal phase is converted into the thermodynamically favoured monoclinic phase. Formation of metastable tetragonal zirconia has been rationalized on the basis of surface strain energy [44]. When amorphous zirconium hydroxide is treated with sulfate-ions, the sulfate groups generally influence to relieve the surface strain energy thereby stabilizing the tetragonal phase. They are also known to prevent increase of crystallite size to reach a critical diameter necessary to favour the monoclinic phase [45]. The total acidity of the samples was measured using ammonia-TPD technique. The results revealed two temperature maximum on both the samples indicating the presence of two different types of acid sites with different acid strength distribution. The temperature of desorption maximums were more in the case of sulfate-ion promoted sample indicating stronger acid sites. The total amount of ammonia desorbed in the case of sulfated sample is much larger than that of the unpromoted ZrO_2 (Table 1). It clearly indicates that impregnated sulfate-ions show a strong influence on the acidic properties of the zirconia.

The catalytic activity of sulfate-ion promoted ZrO_2 was investigated for the Knoevenagel condensation by employing various aliphatic, aromatic and hetero-aromatic aldehydes with malononitrile as active methylene compound and presented in Table 2. All reactions investigated were almost completed in 0.5–6.0 h duration to produce the corresponding electrophilic alkenes with 78–98% yield. Hetero-aromatic aldehydes, such as furfural and pyridine-4-carboxaldehyde provided very good yields. Aromatic aldehydes with electron withdrawing groups ($-\text{NO}_2$, $-\text{CN}$) also offered good yields and the reactions were completed in short times. Also in the case of electron donating groups ($-\text{OH}$, $-\text{OCH}_3$, $-\text{CH}_3$), reasonably good yields were observed but demanded little more reaction time. In the similar way aliphatic aldehydes also took more reaction time due to their less reactivity. In the case of 2- and 4-nitro benzaldehydes, latter gave more yield than the former due to steric hindrance. The conjugated aldehyde was also converted into olefin in short period of time without the formation any side product. The unpromoted ZrO_2 sample exhibited negligible activity under the identical reaction conditions, which clearly signifies the involvement of

strong acid sites in the reaction. Reusability of the catalyst was investigated by carrying out repeated runs on the same batch of the used catalyst. After the completion of reaction, the wet catalyst was washed with dichloromethane, dried and recycled. No appreciable change in the activity was observed for 3–4 runs.

4. Conclusions

The following conclusions can be drawn from this study: (1) Incorporation of sulfate-ions into the hydrous zirconia and subsequent calcination at 923 K show a significant influence on the physicochemical properties of the ZrO_2 . (2) Metastable tetragonal ZrO_2 phase with smaller crystallites dominates over the monoclinic phase with larger crystallites in the case of sulfate-ion promoted catalyst. (3) Impregnated sulfate-ions also enhance the specific surface area and total number of acid sites of the ZrO_2 . (4) The sulfate-ion promoted ZrO_2 exhibits excellent catalytic activity for Knoevenagel condensation of various aliphatic, aromatic and heterocyclic aldehydes with malononitrile. Most importantly this catalyst facilitates the reaction under solvent-free conversions and exhibits good recycling capacity. (5) This study establishes about another possible application for sulfate-ion promoted ZrO_2 catalyst in organic synthesis and transformation reactions.

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References

- [1] G. Jones, *Inorganic Reactions*, vol. 15, Wiley, New York, 1967, p. 204.
- [2] F. Freeman, *Chem. Rev.* 80 (1980) 329.
- [3] L.F. Tietze, *Chem. Rev.* 96 (1996) 115.
- [4] R.L. Reeves, S. Patai (Eds.), *The Chemistry of Carbonyl Compounds*, Interscience Publishers, New York, 1996, p. 567.
- [5] (a) C. Jones, *Org. React.* 15 (1967) 204;
(b) S.A.-E. Ayoubi, F. Texier-Baullet, J. Hamelin, *Synthesis* (1994) 258.
- [6] L.F. Tietze, U. Beifuss, in: B.M. Trost, I. Fleming, C.H. Heathcock (Eds.), *Comprehensive Organic Synthesis*, vol. 2, Pergamon Press, Oxford, 1991, pp. 341–392.
- [7] (a) G. Cardillo, S. Fabbroni, L. Gentilucci, M. Gianotti, A. Tolomelli, *Synth. Commun.* 33 (2003) 1587;
(b) D.S. Acker, W.R. Hertler, *J. Am. Chem. Soc.* 84 (1962) 3370.
- [8] A.V. Narsaiah, A.K. Basak, B. Visali, K. Nagaiah, *Synth. Commun.* 34 (2004) 2893.
- [9] S. Sebti, A. Smahi, A. Solhy, *Tetrahedron Lett.* 43 (2002) 1813.
- [10] D.S. Bose, A.V. Narsaiah, *J. Chem. Res. (S)* (2001) 36.
- [11] (a) J.R. Harjani, S.J. Nara, M.M. Salunkhe, *Tetrahedron Lett.* 43 (2002) 1127;
(b) F.A. Khan, J. Dash, R. Satapathy, S.K. Upadhyaya, *Tetrahedron Lett.* 45 (2004) 3055.
- [12] D. Brunel, *Micropor. Mesopor. Mater.* 27 (1999) 329.
- [13] R.W. Hein, M.J. Astle, J.R. Shelton, *J. Org. Chem.* 26 (1961) 4874.
- [14] H. Moison, F. Texier-Bouillet, A. Foucaud, *Tetrahedron* 43 (1987) 537.
- [15] A. Corma, V. Fornes, R.M. Martin-Aranda, F. Reiy, *J. Catal.* 134 (1992) 58.
- [16] M.J. Climent, A. Corma, V. Fornes, A. Frau, R. Guil-Lopez, S. Iborra, J. Primo, *J. Catal.* 163 (1996) 392.

- [17] U.D. Joshi, P.N. Joshi, S.S. Tamhankar, V.V. Joshi, C.V. Rode, V.P. Shiralkar, *Appl. Catal. A: Gen.* 239 (2003) 209.
- [18] A. Corma, V. Fornes, R.M. Martin-Aranda, H. Garcia, J. Primo, *Appl. Catal.* 59 (1990) 237.
- [19] A. Corma, R.M. Martin-Aranda, *Appl. Catal. A: Gen.* 105 (1993) 271.
- [20] J.O. Metzger, *Angew. Chem. Int. Engl. Ed.* 37 (1998) 2975.
- [21] (a) K. Tanaka, F. Toda, *Chem. Rev.* 100 (2000) 1025;
(b) A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, D. Mathe, *Synthesis* (1998) 1213.
- [22] W. Bao, Y. Zhang, J. Wang, *Synth. Commun.* 26 (1996) 3025.
- [23] O. Attanasi, P. Fillippone, A. Mei, *Synth. Commun.* 13 (1983) 1203.
- [24] P. Shanthan Rao, R.V. Venkatratnam, *Tetrahedron Lett.* 32 (1991) 5821.
- [25] A.V. Narsaiah, K. Nagaiah, *Synth. Commun.* 33 (2003) 3825.
- [26] J.S. Yadav, B.V.S. Reddy, A.K. Basak, B. Visali, A.V. Narsaiah, K. Nagaiah, *Eur. J. Org. Chem.* (2004) 546.
- [27] K. Arata, *Adv. Catal.* 37 (1990) 165.
- [28] B.H. Davis, R.A. Keogh, R. Srinivasan, *Catal. Today* 20 (1994) 219.
- [29] X. Song, A. Sayari, *Catal. Rev. Sci. Eng.* 38 (1996) 329.
- [30] G.D. Yadav, J.J. Nair, *Micropor. Mesopor. Mater.* 33 (1999) 1.
- [31] X. Li, K. Nagaoka, L.J. Simon, J.A. Lercher, S. Wrabetz, F.C. Jentoft, C. Breitkopf, S. Matysik, H. Papp, *J. Catal.* 230 (2005) 214.
- [32] B.M. Reddy, P.M. Sreekanth, V.R. Reddy, *J. Mol. Catal. A: Chem.* 225 (2005) 71.
- [33] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [34] J.H. Clark, *Acc. Chem. Res.* 35 (2002) 791.
- [35] T. Okuhara, *Chem. Rev.* 102 (2002) 3641.
- [36] T. Yamaguchi, *Catal. Today* 20 (1994) 199.
- [37] A. Khodakov, J. Yang, S. Su, E. Iglesia, A.T. Bell, *J. Catal.* 177 (1998) 343.
- [38] M. Scheithauer, R.E. Jentoft, B.C. Gates, H. Knözinger, *J. Catal.* 191 (2000) 271.
- [39] M. Scheithauer, R.K. Grasselli, H. Knözinger, *Langmuir* 14 (1998) 3019.
- [40] C. Morterra, G. Cerrato, S. Ardizzone, C.L. Bianchi, M. Signoretto, F. Pinna, *Phys. Chem. Chem. Phys.* 4 (2002) 3136.
- [41] B.M. Reddy, P.M. Sreekanth, Y. Yamada, T. Kobayashi, *J. Mol. Catal. A: Chem.* 227 (2005) 81.
- [42] D.J. Zaleski, S. Alerasool, P.K. Doolin, *Catal. Today* 53 (1999) 419.
- [43] B.M. Reddy, V.R. Reddy, *J. Mater. Sci. Lett.* 19 (2000) 763.
- [44] R.C. Garvie, M.F. Goss, *J. Mater. Sci.* 21 (1986) 1253.
- [45] C.J. Norman, P.A. Goulding, I. McAlpine, *Catal. Today* 20 (1994) 313.