

**BIFUNCTIONAL OXIDATIVE AND ACIDIC TITANIUM SILICALITE
(TS-1) CATALYSTS FOR ONE POT SYNTHESIS OF
1,2-OCTANEDIOL FROM 1-OCTENE**

DIDIK PRASETYOKO

UNIVERSITI TEKNOLOGI MALAYSIA

BIFUNCTIONAL OXIDATIVE AND ACIDIC TITANIUM SILICALITE
(TS-1) CATALYSTS FOR ONE POT SYNTHESIS OF
1,2-OCTANEDIOL FROM 1-OCTENE

DIDIK PRASETYOKO

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

MARCH 2006

Specially dedicated to:

My mom, dad, wife and daughters

ACKNOWLEDGEMENT

Bismillaahirrahmaanirrohiim

In the name of Allah, the most Gracious, the most Merciful

Alhamdulillahirabbil ‘alamin, Allaahumma sholli ala Muhammad wa ‘ala alihi wa shohbihi wa sallam. All praise must be to Allah, The supreme Lord of the world. Peace and blessing to Rasulullaah Muhammad Shollallahu ‘Alaihi Wasallam, all the prophets, his families, his close friends and all Muslims.

I wish to thank my supervisors, Assoc. Prof. Dr. Zainab Ramli, Assoc. Prof. Dr. Salasiah Endud and Dr. Hadi Nur for their continual guidance, encouragement and patience. Their understanding and supervision are very much appreciated. A research grant from the Ministry of Science Technology and Innovation Malaysia (MOSTI) under grant no. 09-02-06-0057 SR0005/09-03 is gratefully acknowledged.

I also would like to express my gratitude to all lecturers and researchers of the Department of Chemistry for their support and Ibnu Sina Institute for Fundamental Science Studies UTM for catalysts characterizations. I would also like to thank Prof. Dr. Gopinathan Sankar from Davy-Faraday Research Laboratory for helpful discussion on the TS-1. Thanks to all the laboratory assistants and friends in the Department of Chemistry for their kindness and wonderful cooperation.

Last but not least, I am grateful to my father and mother: Saderi and Soegijarni, my father and mother in law: Muhamad Nafik and Ninik Supini, my wife: Vivin Navijanti, my daughters: Dini Viandi Ramadhani, Nabilah Amanina, Izzah Firzanah and Afa Taqiya, and my brother and sisters: Rini Ekowati, Setyo Nugroho and Eni Puji Lestari for their prayer, love, understanding, encouragement and support.

ABSTRACT

New bifunctional catalysts containing both oxidative and Brønsted acidic sites have been prepared and used for the consecutive transformation of alkenes to the corresponding diols via the formation of epoxides with aqueous hydrogen peroxide as oxidant. The catalytic system was designed in order such that two kinds of active sites would allow for the epoxidation of alkenes to take place within the pore channels of titanium-containing molecular sieve while acid catalysis of the epoxides to diols occurs on the external surface of the catalyst. Based on this design, titanium silicalite (TS-1), an excellent and commercial oxidation catalyst known so far, has been chosen. The TS-1 was then modified with different acidic oxide precursors. Synthesis of the series of bifunctional catalysts was achieved by deposition of various loadings of acidic oxide precursors up to 25 wt% onto TS-1 powder. The Ti^{4+} and acidic oxides in the TS-1 molecular sieve served as oxidative and acidic sites, respectively. The thus obtained bifunctional catalysts were sulfated TS-1 ($\text{SO}_4^{2-}/\text{TS-1}$), sulfated titanium oxide supported on TS-1 ($\text{SO}_4^{2-}\text{-Ti}/\text{TS-1}$), tungsten oxide supported on TS-1 ($\text{WO}_3/\text{TS-1}$), sulfated zirconia supported on TS-1 ($\text{SZ}/\text{TS-1}$), and niobium oxide supported on TS-1 ($\text{Nb}/\text{TS-1}$). The X-ray diffraction analysis revealed that TS-1 still retained the MFI structure after incorporation of the acidic oxides even when the crystallinity is lower. The infrared (IR) and ultra-violet diffuse reflectance (UV-Vis DR) spectra showed that the titanium in TS-1 was mainly in tetrahedral coordination after incorporation of acidic oxides. Results of pyridine adsorption followed by IR spectroscopy showed the presence of Brønsted acid sites in $\text{WO}_3/\text{TS-1}$, $\text{Nb}/\text{TS-1}$ and highly loaded $\text{SZ}/\text{TS-1}$ but not sulfated samples of TS-1 ($\text{SO}_4^{2-}/\text{TS-1}$ and $\text{SO}_4^{2-}\text{-Ti}/\text{TS-1}$). In the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane, all the catalysts showed a significant increase in the rate of formation of 1,2-epoxyoctane with respect to TS-1. The presence of acidic oxides in TS-1 was proposed to explain the increased hydrophilic character of the catalysts, which is responsible for the higher rate of formation of reactive oxo-titanium species. Moreover, the acid sites were shown to effectively catalyze the formation of 1,2-octanediol with the 10 wt% niobium oxide supported on TS-1 giving the highest yield. Comparison of the catalytic performance of the prepared bifunctional catalysts with that of the mechanical mixture comprising of TS-1 and H-ZSM-5 (Brønsted acid), showed that the bifunctional catalysts were more active; suggesting that specific location of the two active sites plays an important role in the consecutive transformation of alkenes to epoxides and then diols. The higher activity of the bifunctional catalysts was supposedly due to the location of the acidic sites in the immediate vicinity of the oxidative sites which enabled the epoxidation products to undergo hydrolysis rapidly at the Brønsted acid sites that were located on the external surface of TS-1.

ABSTRAK

Mangkin dwifungsi baru yang mengandung kedua-dua tapak pengoksidaan dan tapak asid Brønsted telah disediakan dan digunakan dalam tindak balas penukaran berturutan alkena kepada diol melalui pembentukan epoksida dengan menggunakan hidrogen peroksida sebagai agen pengoksidaan. Sistem mangkin direka bentuk supaya mempunyai dua jenis tapak aktif yang membolehkan tindak balas pengepoksidaan alkena berlaku di dalam liang penapis molekul yang mengandungi titanium, manakala pemangkinan asid daripada epoksida kepada diol berlaku pada permukaan luar mangkin. Berdasarkan kepada reka bentuk sistem mangkin ini, titanium silikalit (TS-1) yang merupakan mangkin pengoksidaan komersial yang sangat baik pada masa kini, telah dipilih sebagai tapak pengoksidaan bagi mangkin dwifungsi. Seterusnya mangkin TS-1 diubahsuai dengan pelbagai bahan pemula oksida asid. Suatu siri mangkin dwifungsi disintesis dengan memasukkan pelbagai peratus muatan oksida asid sehingga 25 wt% pada TS-1. Ti^{4+} dan oksida asid pada penapis molekul TS-1 masing-masing berfungsi sebagai tapak pengoksidaan dan asid. Mangkin dwifungsi yang terhasil ialah TS-1 tersulfat ($SO_4^{2-}/TS-1$), titanium oksida tersulfat berpenyokong TS-1 ($SO_4^{2-}-Ti/TS-1$), tungsten oksida berpenyokong TS-1 ($WO_3/TS-1$), zirconia tersulfat berpenyokong TS-1 ($SZ/TS-1$), dan niobium oksida berpenyokong TS-1 ($Nb/TS-1$). Analisis XRD telah mengesahkan bahawa TS-1 masih mengekalkan struktur MFI selepas penambahan pemula oksida asid, walaupun keahablurannya lebih rendah. Spektrum inframerah (IR) dan UV-Vis DR menunjukkan bahawa titanium dalam TS-1 terkoordinat dalam bentuk tetrahedral selepas penambahan oksida asid. Hasil penjerapan piridina diikuti spektroskopi IR telah menunjukkan kehadiran tapak asid Brønsted pada $WO_3/TS-1$, $Nb/TS-1$, dan $SZ/TS-1$, tetapi tidak pada sampel TS-1 tersulfat ($SO_4^{2-}/TS-1$ dan $SO_4^{2-}-Ti/TS-1$). Dalam tindak balas berturutan bermula dari 1-oktena kepada 1,2-oktanadiol melalui pembentukan 1,2-epoksioktana, semua mangkin menunjukkan kadar pembentukan 1,2-epoksioktana lebih cepat berbanding TS-1. Kehadiran oksida asid pada TS-1 dicadangkan telah meningkatkan sifat hidrofilik mangkin, yang seterusnya menyebabkan peningkatan kadar pembentukan spesies reaktif oksotitanium. Tapak asid telah menunjukkan sifat pemangkinan yang efektif dalam pembentukan 1,2-oktanadiol, dengan 10 wt% niobium oksida berpenyokong TS-1 memberikan peratus hasil tertinggi. Perbandingan kemampuan mangkin dwifungsi dan mangkin dengan campuran mekanikal daripada TS-1 dan H-ZSM-5 (asid Brønsted), menunjukkan bahawa mangkin dwifungsi lebih aktif, mencadangkan lokasi yang spesifik bagi kedua-dua tapak aktif memainkan peranan penting dalam tindak balas berturutan daripada alkena kepada epoksida dan seterusnya diol. Aktiviti mangkin dwifungsi yang tinggi dicadangkan disebabkan oleh kedudukan tapak asid yang berdekatan dalam kawasan tapak pengoksidaan, yang memungkinkan hasil pengepoksidaan terhidrolisis dengan cepat pada tapak asid Brønsted yang terdapat pada luar permukaan mangkin TS-1.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF SYMBOL / ABBREVIATIONS	xx
	LIST OF PUBLICATIONS	xxi
1	INTRODUCTION	
	1.1 Background of Study	1
	1.2 Design of Bifunctional Oxidative and Acidic Catalyst	4
	1.3 Objectives of the Study	6
	1.4 Scope of the Study	6

2	LITERATURE REVIEW	
2.1	Bifunctional Oxidative and Acidic Catalyst	8
2.2	Titanium Silicalite Molecular-sieves	10
2.2.1	Molecular Structure of TS-1	11
2.2.2	Synthesis of TS-1	15
2.2.3	Catalysis by TS-1	17
2.3	Metal Oxides as Solid Acid Catalysts	20
2.4	Modifications of Silica Based Molecular-sieves	22
3	SYNTHESIS, CHARACTERIZATION AND ACTIVITY OF TITANIUM-SILICALITE MOLECULAR SIEVES	
3.1	Introduction	25
3.2	Experimental	26
3.2.1	Materials Preparation	26
3.2.2	Characterization	28
3.2.3	Catalytic Test	30
3.3	Results and Discussion	30
3.3.1	X-ray Diffraction	30
3.3.2	Infrared Spectroscopy	33
3.3.3	Ultra Violet - Visible Diffuse Reflectance Spectroscopy	35
3.3.4	Temperature Programmed Desorption of Ammonia	39
3.3.5	Hydroxyl Groups and Acidic Sites	41
3.3.6	Epoxidation of 1-Octene	45

4	SULFATED TITANIUM SILICALITE	
4.1	Introduction	50
4.2	Experimental	51
4.2.1	Preparation of Sample	51
4.2.2	Characterizations	53
4.3	Results and Discussion	54
4.3.1	Structure Characterization	54
4.3.2	Acidity Studies	62
4.3.3	Catalytic Activity	65
5	TUNGSTEN OXIDE ON THE SURFACE OF TITANIUM SILICALITE	
5.1	Introduction	69
5.2	Experimental	70
5.2.1	Preparation of Sample	70
5.2.2	Characterizations	71
5.3	Results and Discussion	72
5.3.1	X-ray Diffraction	72
5.3.2	Infrared Spectroscopy	75
5.3.2.1	Hydroxyl Stretching Region	75
5.3.2.2	Framework Vibration Region	78
5.3.3	UV - Visible Diffuse Reflectance Spectroscopy	82
5.3.4	Temperature Programmed Reduction	83
5.3.5	Acidity	87
5.3.6	Catalytic Test	89

6	SULFATED ZIRCONIA DISPERSED ON TITANIUM SILICALITE	
6.1	Introduction	95
6.2	Experimental	96
6.2.1	Preparation of Sample	96
6.2.2	Characterizations	98
6.2.3	Catalytic Activity	98
6.3	Results and Discussion	99
6.3.1	Structure and Acidity of SZ from Zirconium Sulfate	99
6.3.1.1	X-ray Diffraction	99
6.3.1.2	Temperature Programmed Reduction	102
6.3.1.3	UV-Visible Diffuse Reflectance Spectroscopy	105
6.3.1.4	Infrared Spectroscopy	106
6.3.1.5	Acidity	110
6.3.2	Sulfated Zirconia Dispersed on the TS-1 (SZ/TS-1)	116
6.3.2.1	X-ray Diffraction	116
6.3.2.2	Infrared Spectroscopy	118
6.3.2.3	UV-Visible Diffuse Reflectance Spectroscopy	120
6.3.2.4	Temperature Programmed Reduction	121
6.3.2.5	Acidity	123
6.3.3	Catalytic Activity	131

7	NIOBIC ACID DISPERSED OVER TITANIUM SILICALITE	
7.1	Introduction	136
7.2	Experimental	137
7.2.1	Preparation of Sample	137
7.2.2	Characterizations	139
7.3	Results and Discussion	140
7.3.1	X-ray Diffraction	140
7.3.2	Infrared Spectroscopy	142
7.3.3	UV-Visible Diffuse Reflectance Spectroscopy	143
7.3.4	Temperature Programmed Reduction	146
7.3.5	Hydroxyl Groups	149
7.3.6	Acidity Study	151
7.3.7	Catalytic Activity	157
8	SUMMARY OF THE ACTIVITY OF BIFUNCTIONAL OXIDATIVE AND ACIDIC CATALYSTS	162
9	CONCLUDING REMARKS	166
	REFERENCES	169
	PUBLICATIONS	191

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Types and numbers of catalysts used in industrial processes (Tanabe and Hölderich, 1999).	20
2.2	The acid strength of zeolites in water (Paze <i>et al.</i> , 1998).	21
2.3	Acid sites on various transition metal oxides determined by ammonia or pyridine adsorption (Kung, 1989).	22
3.1	Chemical composition and method of preparation	27
3.2	Structure and crystallinity of samples by X-ray diffraction technique	31
3.3	Infrared wavenumber of the samples	33
3.4	The number and strength of acid sites in the samples	39
3.5	Amount of Brønsted and Lewis acid sites of the samples on the basis of pyridine absorption, after evacuation at 150°C	45
4.1	Initial titanium compositions of the samples	53
4.2	The highest peak intensity and phases of the samples	57
4.3	The percentage of tetrahedral titanium based on TS-1 and band positions in the UV-Vis DR spectra	60
4.4	Acid strength by Hammet indicator	63
4.5	Amount of Lewis acid sites (1445 cm^{-1}) of the samples	65
4.6	The yield of 1,2-octanediol from epoxidation of 1-octene using H_2O_2 as oxidant after 48 h.	68
5.1	Amount of WO_3 loading of the samples using neutral preparation conditions and TS-1 as support	71
5.2	The amount of the Brønsted and Lewis acid sites of the samples	89

5.3	The 1-octene conversion in the epoxidation reaction with H ₂ O ₂ at 70°C catalyzed by TS-1 and WO ₃ /TS-1	90
5.4	Catalytic activity of the WO ₃ /TS-1 in the epoxidation of 1-octene with H ₂ O ₂ at 70°C for 48 h	94
6.1	Zirconium content and preparation condition of the samples	97
6.2	Reduction temperature and hydrogen consumed of the samples	104
7.1	Chemical compositions of the samples and preparation method	138
7.2	Structure and crystallinity of samples	142
7.3	The amount of the Brønsted and Lewis acid sites and the area under the peak at around 1490 cm ⁻¹ of the samples	155
7.4	Catalytic activity of the Nb/TS-1 in the epoxidation of 1-octene with H ₂ O ₂ at 70°C for 48 h	158

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Oxidative and acidic catalyst for consecutive oxidation and acid catalytic reactions	5
1.2	Methodology of research	7
2.1	Epoxidation of alkenes to epoxide and consecutive acid catalyzed reactions (van der Wall <i>et al.</i> 1998).	10
2.2	The features of MFI type zeolite: (1) crystal morphology; (2) pore section; (3) part of the crystal structures; (4) detail of the atomic structure (Cundy and Cox, 2003).	12
2.3	Location of titanium in the TS-1 structure (Henry <i>et al.</i> 2001).	13
2.4	Pore system in the zeolite beta. (a) Periodic Building Unit seen along the plane normal, (b) Cell content in *BEA seen along <i>b</i> (left) and <i>a</i> (right) (Baerlocher <i>et al.</i> , 2001).	14
2.5	Structure of MCM-41 shows distance between the pore = 3.5 nm, amorphous wall structure and hexagonal pore (Gusev, 1998).	14
2.6	Some examples of reagent mixtures for TS-1 preparation. TEOS(T): tetraethyl orthosilicate (titanate); TB(P)OT: tetrabutyl (propyl) orthotitanate; TPA ⁺ : tetrapropyl ammonium; TB(E)A ⁺ : tetrabutyl (ethyl) ammonium; TB(E)P ⁺ : tetrabutyl (ethyl) phosphonium	16
2.7	Types of reactions catalyzed by TS-1 (Katz, 1999).	19
3.1	Experimental setup for hydroxyl groups and acidity analysis	29
3.2	XRD pattern of the TiO ₂ , silicalite, ZSM-5 and TS-1 samples	32
3.3	FTIR spectra of the TiO ₂ , silicalite, ZSM-5 and TS-1 samples	34

3.4	Infrared spectra of TS-1 samples in the region of 1000 – 700 cm ⁻¹ and the intensity ratio of peak at about 970 to 800 cm ⁻¹	36
3.5	UV-vis DR spectra of the TiO ₂ , silicalite, ZSM-5 and TS-1 samples	37
3.6	The relationships between concentration of titanium in the tetrahedral coordination (peak at 215 nm) and amount of titanium in the initial gel (%mol)	38
3.7	TPD-NH ₃ thermogram of the silicalite, ZSM-5 and TS-1 samples	40
3.8	Infrared spectra of the silicalite, ZSM-5 and TS-1 samples in the hydroxyl groups region, after evacuation at 400°C in vacuum	42
3.9	Infrared spectra of the samples after evacuation at 400°C in vacuum followed by pyridine adsorption at room temperature and desorption at 150°C for one hour	44
3.10	The interaction between tetrahedral titanium and pyridine molecule	45
3.11	Yield of 1-octene epoxidation using H ₂ O ₂ at 70°C catalyzed by TS-1 with various titanium contents	46
3.12	Relation between tetrahedral titanium content (IR data) and catalytic activity (yield of 1,2-epoxyoctane for 6 hours of reaction time) of the samples	47
3.13	Reactive oxygen species in the titanosilicates (Chaudari <i>et al.</i> , 2001).	48
3.14	The effect of reaction mixture addition to the rate of formation of 1,2-epoxyoctane. Conditions: 5 mmol 1-octene in 5 g acetone, 7 mmol H ₂ O ₂ , catalyst: 0.025 g TS-1 (1%) at 70°C. [A]. 1-octene + H ₂ O ₂ + TS-1, [B]. 1-octene + TS-1 + H ₂ O ₂ , and [C]. TS-1 + H ₂ O ₂ + 1-octene	49
4.1	TPR profiles of the SO ₄ ²⁻ /TS-1 and SO ₄ ²⁻ -Ti/TS-1 samples	55
4.2	XRD pattern of the TS-1, sulfated TS-1 and sulfated titanium TS-1	56
4.3	Infrared spectra of the TS-1, sulfated TS-1 and sulfated titanium TS-1	58

4.4	UV-Vis DR spectra of the ZSM-5, TS-1, SO ₄ ²⁻ /TS-1 and SO ₄ ²⁻ -Ti/TS-1 samples	60
4.5	FTIR spectra of the TS-1, SO ₄ ²⁻ /TS-1 and SO ₄ ²⁻ -Ti/TS-1 samples after heated at 400°C for 4 h in vacuum	62
4.6	Infrared spectra of the samples after following treatments: heating at 400°C for 4 h in vacuum, adsorbed pyridine at room temperature, and desorption pyridine at 150°C for an hour	64
4.7	The yield of 1,2-epoxyoctane on the epoxidation of 1-octene using TS-1, SO ₄ ²⁻ /TS-1 and SO ₄ ²⁻ -Ti/TS-1	66
4.8	Proposed model of the local environment structure of Ti; (a) bipodal, (b) tetrapodal and (c) tripodal	66
5.1	XRD patterns of the TS-1 and tungsten-coated TS-1 samples	73
5.2	The WO ₃ content vs. XRD peak intensity ratio of WO ₃ to TS-1 in the samples	75
5.3	Infrared spectra in the range of hydroxyl groups observation for titanium silicalite samples with different WO ₃ content	76
5.4	The WO ₃ content vs ratio of the IR peak area at 3726 cm ⁻¹ to 1880 cm ⁻¹ and 3505 cm ⁻¹ to 1880 cm ⁻¹ in the samples	78
5.5	The framework vibration of the TS-1 and tungsten-coated TS-1 samples	80
5.6	The WO ₃ content vs ratio of the IR peak area at the range 900-700 cm ⁻¹ to 548 cm ⁻¹ in the samples	81
5.7	UV-Visible DR spectra of TS-1, WO ₃ , and WO ₃ /TS-1 samples	83
5.8	TPR profiles of WO ₃ /TS-1 samples	85
5.9	Correlation between WO ₃ content and hydrogen consumed of the samples	86
5.10	Infrared spectra of the samples after evacuation at 400°C in vacuum followed by pyridine adsorption at room temperature and desorption at 150°C for one hour	88
5.11	The yield of 1,2-epoxyoctane from 1-octene epoxidation using H ₂ O ₂ at 70°C catalyzed by TS-1 and WO ₃ /TS-1	91
5.12	The yield of 1,2-octanediol from 1-octene epoxidation of using H ₂ O ₂ at 70°C catalyzed by TS-1 and WO ₃ /TS-1	93

5.13	The yield of 1,2-octanediol at 48 h of reaction time and the ratio of 1,2-octanediol to the amount of Brønsted acid sites in various catalysts	94
6.1	XRD pattern of the $Zr(SO_4)_2$ calcined at the various temperature for 6 h	101
6.2	Diffraction line intensity of tetragonal and monoclinic phases, and its ratio	102
6.3	TPR profiles of the samples zirconia free-sulfate and zirconium sulfate calcined at various temperatures	103
6.4	UV-Vis DR spectra of the samples SZ at various calcination temperature	106
6.5	Infrared spectra in the sulfate region of the zirconium sulfate calcined at the temperature 500, 600 and 700°C for 6 h.	108
6.6	Infrared spectra of self-supported wafer of the zirconium sulfate calcined at the temperature 500, 600 and 700°C for 6 h in the hydroxyl region	109
6.7	Infrared spectra in the hydroxyl region of the zirconium sulfate samples after pyridine adsorption	110
6.8	Infrared spectra of the samples after following treatments: evacuation at 400°C, pyridine adsorption at room temperature, and desorption at 150°C for 1 h	113
6.9	Amount of Brønsted (B; 1545 cm^{-1}) and Lewis (L; 1444 cm^{-1}) acid sites calculated by pyridine adsorption, and $\Delta_{S=O}$ for the sample zirconium sulfate calcined at different temperatures	114
6.10	Infrared spectra of the sample SZ500 after evacuation at different temperature at 150, 300 and 400°C for 1 h	115
6.11	XRD pattern of the SZ500 and SZ/TS-1 samples	117
6.12	The graph of peak intensity of TS-1 at $2\theta=23^\circ$ vs loading amount of zirconium on the samples	118
6.13	Infrared spectra of the samples in the framework region	119
6.14	UV-Visible DR spectra of the samples	121
6.15	TPR profiles of samples	122

6.16	FTIR spectra of the SZ/TS-1 samples after evacuation at 400°C for 4 h in vacuum condition	124
6.17	FTIR spectra of the SZ/TS-1 samples in the pyridine and sulfate region	125
6.18	FTIR spectra of the SZ/TS-1 samples after pyridine adsorption and evacuation at 150°C for 1 h. in the hydroxyl region	127
6.19	FTIR spectra of the SZ/TS-1 samples after pyridine adsorption and evacuation at 150°C for 1 h. in the pyridine and sulfate regions	128
6.20	Amount of Brønsted and Lewis acid sites of the samples SZ/TS-1 calculated based on the pyridine peak after evacuation at 150°C for 1 h	129
6.21	FTIR spectra of the sample 20SZ/TS-1. (A). after evacuation at 400°C for 6 h., (B). after pyridine adsorption and evacuation at 150°C for 1 h., (C). after evacuation at 300°C, and (D). after evacuation at 400°C	130
6.22	The yield of 1,2-epoxyoctane from reaction of 1-octene epoxidation using H ₂ O ₂ as oxidant in the solvent acetone at 70°C catalyzed by various contents of zirconium sulfate-promoted TS-1	132
6.23	The yield of 1,2-octanediol from reaction of 1-octene epoxidation using H ₂ O ₂ as oxidant in the solvent acetone at 70°C catalyzed by various contents of zirconium sulfate-promoted TS-1	134
6.24	The Proposed model of TS-1 loaded with sulfated zirconia as bifunctional catalyst for consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane	135
7.1	XRD pattern of the NBA, NBO, TS-1 and XNb/TS-1 samples	141
7.2	FTIR spectra of the NBA, NBO, TS-1 and XNb/TS-1 samples	145
7.3	UV-Vis DR spectra of the NBA, NBO, TS-1 and XNb/TS-1 samples	146
7.4	TPR profiles of the NBA, NBO, TS-1 and XNb/TS-1 samples	148
7.5	FTIR spectra of the samples in the hydroxyls region, after evacuation under vacuum at 200°C	150

7.6	FTIR spectra of the sample 3Nb/TS-1 in the hydroxyls region after evacuation under vacuum at temperature 120, 200 and 400°C	152
7.7	FTIR spectra of the NBA, NBO, TS-1 and XNb/TS-1 samples after evacuation at 200°C for 24 h. followed by pyridine adsorption at room temperature and evacuation at 150°C for one hour, in the pyridine regions	153
7.8	Correlation between the niobium content and the amount of acid sites of the catalysts	155
7.9	The formation of 1,2-epoxyoctane from 1-octene epoxidation using H ₂ O ₂ at 70°C catalyzed by NBA, NBO, TS-1 and XNb/TS-1	159
7.10	The yield of 1,2-octanediol from 1-octene epoxidation of using H ₂ O ₂ at 70°C catalyzed by NBA, NBO, TS-1 and XNb/TS-1	160
7.11	Correlation between the yield of 1,2-octanediol and amount of Brønsted acid sites of the catalysts	161
8.1	The yield of 1,2-octanediol over prepared catalysts	164
8.2	The ratio of the yield of 1,2-octanediol to the amount of Ti ⁴⁺ in the prepared catalysts	165
8.3	Correlation of the selectivity of 1,2-octanediol and the amount of Brønsted acid sites in the prepared catalysts	165

LIST OF SYMBOL / ABBREVIATIONS

FTIR	- Fourier Transform Infrared
GC	- gas chromatography
GC-MSD	- gas chromatography mass spectrometry detector
h	- hour
NBA	- niobium oxide hydrated or niobic acid
NBO	- niobium oxide
SIL	- silicalite
SZ	- sulfated zirconia
TEOS	- tetraethylorthosilicate
TEOT	- tetraethylorthotitanate
TPAOH	- tetrapropylammonium hydroxide
TPD-Ammonia	- Temperature Programmed Desorption of Ammonia
TPR	- Temperature Programmed Reduction
TS-1	- titanium silicalite - 1
UV-Vis DR	- Ultra Violet - Visible Diffuse Reflectance
wt%	- weight %
XRD	- X-ray Diffraction

LIST OF PUBLICATIONS

International Journals:

1. **Didik Prasetyoko**, Salasiah Endud, Halimaton Hamdan, Zainab Ramli, and Bogdan Sulikowski. "Crystalline Silica of the Rice Husk Ash is Transformed into Zeolite Beta". *Waste Management*. Accepted, September 16, 2005.
2. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. "TS-1 Loaded with Sulfated Zirconia as Bifunctional Oxidative and Acidic Catalysts for Transformation of 1-Octene to 1,2-Octanediol". *Journal of Molecular Catalysis A. Chemical*. 241: 118-125, 2005.
3. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. "Preparation and Characterization of Bifunctional Oxidative and Acidic Catalysts Nb₂O₅/TS-1 for Synthesis of Diols". *Materials Chemistry and Physic*. 93: 443-449, 2005.
4. **Didik Prasetyoko**, Salasiah Endud, Zainab Ramli and Hadi Nur. "Enhancement of Catalytic Activity of Titanosilicalite-1 – Sulfated Zirconia Combination Towards Epoxidation of 1-Octene with Aqueous Hydrogen Peroxide". *Reaction Kinetics and Catalysis Letters*. 86(1): 83-89, 2005.
5. Hadi Nur, **Didik Prasetyoko**, Salasiah Endud, and Zainab Ramli. "Sulfation: a Simple Method to Enhance the Catalytic Activity of TS-1 in Epoxidation of 1-Octene with Aqueous Hydrogen Peroxide". *Catalysis Communications*. 5: 725-728, 2004.
6. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. "Structural and Superacidity Study of Bifunctional Catalyst, Sulfated-Titanium/TS-1". *Malaysian Journal of Chemistry*. 7(1): 011-018, 2005.

Conference and National Publications:

1. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. “Structural and acidity studies of sulfated zirconia prepared from zirconium sulfate”. *Submitted to Majalah IPTEK - ITS*, June 2005.
2. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. “Niobic Acid Dispersed on the Surface of TS-1: Acidity Study”. *Seminar Nasional Kimia*. 9 August 2005. Surabaya, Indonesia.
3. Zainab Ramli, **Didik Prasetyoko**, Salasiah Endud, and Hadi Nur. “Characterization of Bifunctional Oxidative and Acidic Catalyst, Zirconium Sulfate Loaded Titanium Silicalite”. *The XXI Regional Conference on Solid State Science & Technology (RCWSST)*, 10-13 October 2004. Sabah, Malaysia.
4. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. “Preparation and Characterization of Bifunctional Oxidative and Acidic Catalysts Nb/TS-1”. *International Conference on X-Ray Applications in Research & Industry (ICXRI)*, 14-15 September 2004. Pulau Pinang, Malaysia.
5. Zainab Ramli, **Didik Prasetyoko**, Salasiah Endud, and Hadi Nur. “Monolayer Coverage and Acidity Study of Bifunctional Oxidative Acidic Catalyst by Infrared Spectroscopy: Zirconia Sulfate Loaded Titanium Silicalite”. *Simposium Kimia Analisis Malaysia (SKAM-17)*. 24-26 August 2004. Pahang, Malaysia.
6. **Didik Prasetyoko**, Zainab Ramli, Salasiah Endud, and Hadi Nur. “A New Approach to Probe the Dispersion Capacity of Tungsten Oxide on the Surface of Titanium Silicalite by Infrared Spectroscopy”. *Annual Fundamental Science Seminar (AFSS)*, 2004. Johor Bahru, Malaysia.

CHAPTER 1

INTRODUCTION

Catalysis is an important process to improve the production of chemicals. This phenomenon can be employed in a chemical reaction that is favored thermodynamically but is very slow without the use of a catalyst. The catalyst accelerates the kinetics of the reaction to attain equilibrium without being consumed in the process. It plays an essential role in the manufacture of a wide range of products, from gasoline and plastics to fertilizers and herbicides, which would be unobtainable or expensive.

There are homogeneous and heterogeneous systems in the catalytic processes. In general, heterogeneous systems offer easier separation of catalysts from the product mixture, reusability of the catalysts and the possibility of continuous processing. On the other hand, homogeneous catalysis usually allows more efficient heat transfer and milder operating condition, as well as higher selectivity. Heterogeneous catalysts are being increasingly studied for liquid and gas phase catalysis.

1.1 Background of Study

A large segment of the modern chemical industry is based on selective catalytic oxidation processes (Centi *et al.*, 2001). More than 60% of the chemicals and intermediates synthesized via catalytic processes are the products of oxidation.

Most of the oxidation processes are being carried out in the gas and liquid phases. Catalytic oxidation in the liquid phase is widely used in bulk chemicals manufacture and are becoming increasingly important in the synthesis of fine chemicals (Sheldon and Dakka, 1994). Catalytic oxidations in the liquid phase generally employ soluble metal salts or complexes as catalysts, oxidants such as O₂, H₂O₂, organics hydro peroxide, and solvents (Centi *et al.*, 2001).

An early example of the successful application of the site-isolation concept in liquid phase oxidation catalysis is the Ti(IV)/SiO₂ catalyst, commercialized by Shell in the 1970s for the production of propene oxide (Sheldon, 1980). Another benchmark was the development of titanium silicalite (TS-1) by Enichem scientists in the mid-eighties (Taramasso *et al.*, 1983). Over the last decade, TS-1 has shown excellent catalytic activity in organic oxidation reactions using hydrogen peroxide as oxidant under mild conditions. In alkenes epoxidation, many works have been done to enhance the epoxide selectivity due to the industrial importance of epoxides in the synthesis of organic and pharmaceutical materials. The ability of TS-1 to catalyze a wide variety of oxidation transformations including alkenes epoxidation with 30% aqueous hydrogen peroxide has led to extensive research worldwide on the synthesis of related heterogeneous catalysts for liquid-phase oxidation (Perego *et al.*, 2001).

Beside the oxidative catalysts, the acid catalysts also play important role in the area of catalysis. There are a number of reactions catalyzed by acid catalysts, i.e. esterification, oligomerization, alkylation, acylation, isomerization, cracking, hydrolysis, and other reactions in the synthesis of intermediates or specialty fine chemicals. Researchers have tried to substitute homogeneous catalysts (HCl, HF, H₂SO₄ and AlCl₃) by heterogeneous solid acid catalysts. The advantages of using heterogeneous acid catalysts is to overcome the problems encountered by homogeneous catalysts, i.e. corrosive, toxic, difficulties in the storage and handling, and environment problem for disposal. The heterogeneous acid catalysts include alumina, zeolites, solid phosphoric acid, cationic ion exchange resin and metal oxides. Some examples of recent successfully commercialized new solid acid catalysts have been reviewed (Mitsutani, 2002).

The two types of catalysts mentioned above are just for oxidative or acidic catalyzed reactions. It means that for a certain type of reaction, certain type of catalysts should be used. Unfortunately, two or three steps of catalytic processes are needed in the production of fine chemicals. Consequently, two reactors with different catalysts and processes should be built and run successively when the product is catalyzed by two catalysts. To overcome such problem, research has been carried out in the design of a new concept in the material catalyst, called bifunctional or multifunctional catalysts, in which two or more active sites are present in one solid material. By using this concept, the whole process is more practical and economical than the two-step processes (Hoelderich, 2000).

One of the crucial points for the development of catalysts is to design the active sites for catalytic processes. The efficiency of a catalytic process in general greatly depends on the performance of the catalyst, rendering the development of efficient catalytic materials one of the foremost challenges in catalysis research. In many of catalytic processes a stream of reactant is passed over tiny particles (atomic or cluster) of active sites on an oxide support surface. One of the challenges is to design highly-functionalized catalysts by a combination of oxidative and acidic active sites for consecutive oxidation and acid catalytic reactions. As shown by the model reaction in Figure 1.1, Ti site acts as oxidative site for oxidation of 1-octene to 1,2-epoxyoctane (as intermediate) and niobic acid acts as acidic site for transformation of 1,2-epoxyoctane to 1,2-octanediol.

Several bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al^{3+} , B^{3+} , Fe^{3+} , Ga^{3+}) and titanium ion (Ti^{4+}) together in the framework of silica based molecular-sieves (Trong On *et al.*, 2003; van der Wall *et al.*, 1998; Krijnen *et al.*, 1999). The catalysts being active both in the oxidation reactions due to the presence of tetrahedral Ti^{4+} and in acid catalyzed reactions as the substitution of the trivalent cations in the framework of silica generates acid sites. In a previous study, some research groups (van der Wall *et al.*, 1998; Davies *et al.*, 2001; Sashidaran *et al.*, 2002) have demonstrated that Ti-Al-beta and Ti-beta zeolites can lead to acid-catalyzed consecutive reaction. The catalysts were active in epoxidation of alcohol or bulky alkenes and selective in diol formation.

Diols products are useful intermediates in the production of pharmaceutical, pesticide, fragrance and other fine chemicals. Diols contribute to high water solubility, hygroscopicity and reactivity with many organic compounds, on usually linear and aliphatic carbon chain. 1,2-octanediol, linear diol containing two primary hydroxyl groups, has bacteriostatic and bactericidal properties which are useful in cosmetics and skin care products as a preservative, an emollient, humectants and wetting agent (Brown *et al.*, 2003; Milbradt *et al.*, 2005). It is also used as an ingredient in inks (Kelly-Rowley and Chatterjee, 2004).

Special 1,2-diols, e.g., ethylene glycol and propylene glycol, are manufactured on a million ton scale per annum. Worldwide production capacities for ethylene glycol in 1995: 9.7 Million ton per annum, while worldwide production of 1,2-propylene glycol in 1994: 1.1 Million ton per annum (Weissermel and Arpe, 2003). A number of 1,2-diols such as 2,3-dimethyl-2,3-butanediol, 1,2-octanediol, 1,2-hexanediol, 1,2-pentanediol, and 1,2- and 2,3-butanediol are interesting for fine chemical applications. At present they are produced in industry by a two-step sequence consisting of epoxidation of the terminal olefin with a peracid followed by hydrolysis of the resulting epoxide (Szmant, 1989; Pohl and Gaube, 1985). In addition, chiral 1,2-diols are of interest as intermediates for pharmaceuticals and agrochemicals (Kolb *et al.*, 1994; Beller *et al.*, 2004).

1.2 Design of Bifunctional Oxidative and Acidic Catalyst

The product selectivity of consecutive oxidation and acid catalytic reactions depends on the nature of the oxidative and acid sites which are located in the structure of zeolite. However, it is difficult to control the number of oxidative sites together with acidic sites in the framework of zeolites. Controlling the number and the location of the active sites is important since it relates to the product selectivity. We have designed an alternative way to prepare bifunctional catalyst containing certain amount of active sites as shown in Figure 1.1.

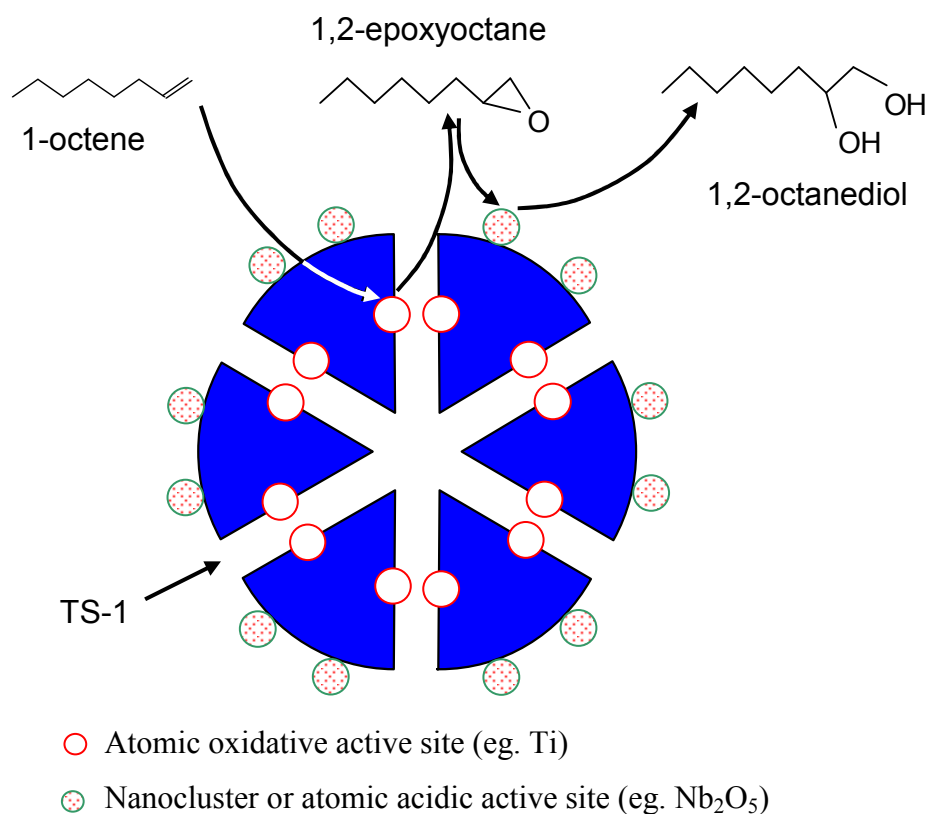


Figure 1.1: Oxidative and acidic catalyst for consecutive oxidation and acid catalytic reactions.

The use of TS-1 as a model catalytic system is an advantage because it is known as a good heterogeneous oxidation catalyst in alkene epoxidation with aqueous hydrogen peroxide as an oxidant. Our proposal is based on the idea that the epoxidation of alkene occurs in the pores of TS-1 and acid catalysis of 1,2-epoxyoctane to 1,2-octanediol takes place on the external surface of TS-1. The location of oxidative and acid sites on the internal and external surfaces of TS-1, respectively, has a beneficial effect in the consecutive oxidation and acid catalytic reactions of 1-octene to 1,2-octanediol (see Figure 1.1) since oxidation and acid reactions preferentially occur in hydrophobic and hydrophilic environments, respectively. It has been reported that the framework of TS-1 has hydrophobic properties (Drago *et al.*, 1998). In order to maintain the hydrophobicity of the TS-1, the acid sites are placed on the external surface of TS-1 which is covered by acidic oxides.

1.3 Objectives of the Study

The objectives of the study are:

1. To prepare and characterize the bifunctional oxidative and acidic catalysts consisting of TS-1 and selected acidic oxides as oxidative and acid sites, respectively.
2. To evaluate the performance of the materials as bifunctional oxidative and acidic catalysts in the one pot synthesis of 1,2-octanediol from 1-octene as a model reaction.
3. To relate the catalytic performance and physicochemical properties of the bifunctional oxidative and acidic catalysts.

1.4 Scope of the Study

Model catalysts with well-defined structural and physicochemical properties serve for elucidating structure-activity relationships (Figure 1.2). The scope of the study is focused on the following aspects i.e. synthesis of titanium silicalite (TS-1) molecular-sieves, preparation of bifunctional oxidative and acidic catalysts, and catalytic testing.

Chapter 3 of this thesis describes the synthesis, characterization and catalytic testing of TS-1. The medium pore microporous material i.e. silicalite and TS-1 were synthesized by hydrothermal method. TS-1 was prepared with various amounts of titanium concentration i.e. 1-4 mol%. Characterizations of the obtained solids were carried out by several techniques, such as X-ray diffraction, infrared and UV-visible diffuse reflectance spectroscopy, temperature programmed desorption and pyridine adsorption followed by infrared spectroscopy.

The bifunctional oxidative and acid catalysts containing certain amount of active sites were prepared by impregnation of sulfated titania, tungsten oxide, sulfated zirconia and hydrated niobium oxide as the acidic precursors on the surface of oxidative TS-1. The structure and physicochemical properties of catalysts were

examined by X-ray diffraction, infrared and UV-visible diffuse reflectance spectroscopy, temperature programmed reduction, and pyridine adsorption. The catalytic performance and structure-activity relationship of bifunctional catalysts were carried out in the consecutive reaction of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane. These studies are reported in four chapters (Chapters 4 to 7).

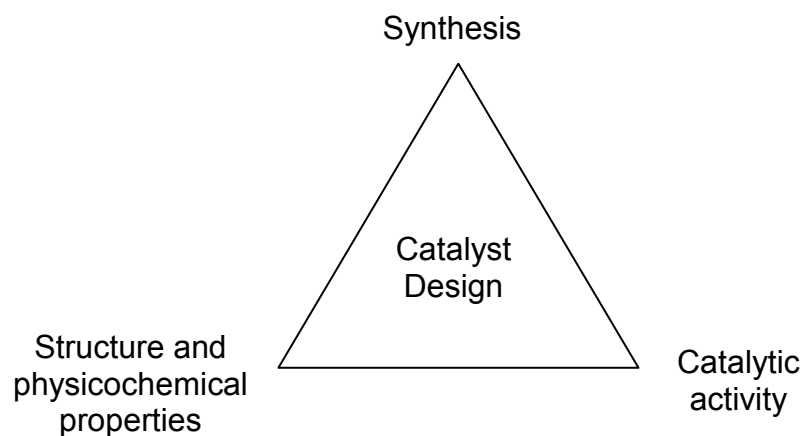


Figure 1.2: Methodology of research.

REFERENCES

- Adeeva, V., Dehaan, J. W., Janchen, J., Lei, G. D., Schunemann, V., Vandeven, L. J. M., Sachtler, W. M. H. and Vansanten, R. A. (1995). Acid Sites in Sulfated and Metal-Promoted Zirconium Dioxide Catalysts. *J. Catal.* 151(2): 364-372.
- Ahmad, I., Dines, T. J., Anderson, J. A. and Rochester, C. H. (1999). Fourier-transform infrared study of the adsorption of acetophenones on niobic acid. *Spectrochimica Acta Part A: Molec. and Biomolec. Spectroscopy* 55(2): 397-409.
- Ahedi, R. K., Shevade, S. S. and Kotasthane, A. N. (1997). Titanosilicate derivative of the NU-1 framework zeolites (TS-NU-1). *Zeolites* 18. 361-367.
- Alvarez-Merino, M.A. Joly, J.P. Carrasco-Marín, F. and Moreno-Castilla C. (2003). Application of ammonia intermittent temperature-programmed desorption to evaluate surface acidity of tungsten oxide supported on activated carbon. *J. Colloid and Interface Science* 260: 449-453.
- Arata, K. (1996). Preparation of superacids by metal oxides for reactions of butanes and pentanes. *Appl. Catal. A: General* 146: 3-32.
- Ardizzone, S. and Bianchi, C. L. (1999). Acidity, sulphur coverage and XPS analyses of ZrO₂-SO₄ powder by different procedures. *Appl. Surface Science* 152: 63-69.
- Armaroli, T., Busca, G., Carlini, C., Giuttari, M., Galletti, A. M. R. and Sbrana, G. (2000). Acid sites characterization of niobium phosphate catalysts and their activity in fructose dehydration to 5-hydroxymethyl-2-furaldehyde. *J. Mol. Catal. A: Chemical* 151(1-2): 233-243.
- Asakura, K. and Iwasawa, Y. (1991). Synthesis, characterization, and catalytic properties of silica-attached one-atomic-layer niobium oxide catalysts. *J. Phys. Chem.* 95(4): 1711-1716.
- Astorino, E., Peri, J. B., Willey, R. J. and Busca, G. (1995). Spectroscopic Characterization of Silicalite-1 and Titanium Silicalite-1. *J. Catal.* 157: 482-500.
- Babou, F., Coudurier, G. and Vedrine, J. C. (1995). Acidic Properties of Sulfated Zirconia: An Infrared Spectroscopic Study. *J. Catal.* 152: 341-349.
- Baerlocher, Ch., Meier, W.M. and Olson, D.H. (2001). Atlas of Zeolite Framework Types, 5th rev. ed., Elsevier, London.

- Barrer, R. M. (1982). Hydrothermal chemistry of zeolites. London: Academic press.
- Barthos, R., Lonyi, F., Onyestyak, G. and Valyon, J. (2000). An IR, FR, and TPD Study on the Acidity of H-ZSM-5, Sulfated Zirconia, and Sulfated Zirconia-Titania Using Ammonia as the Probe Molecule. *J. Phys. Chem. B.* 104: 7311-7319.
- Barton, D. G., Soled, S. L., Meitzner, G. D., Fuentes, G. A. and Iglesia, E. (1999). Structural and Catalytic Characterization of Solid Acids Based on Zirconia Modified by Tungsten Oxide. *J. Catal.* 181(1): 57-72.
- Batamack, P., Vincent R. and Fraissard, J. (1996). The acidity of niobic acid studied by ^1H broad-line NMR at 4 K and H MAS NMR at room temperature: comparison with other solid acids. *Catal. Today* 28(1-2): 31-39.
- Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B. and Schlenker, J. L. (1992). A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates. *J. Am. Chem. Soc.* 114: 10834-10843.
- Beller, M., Dobler, C., Mehlretter, G. and Sundermeier, U. (2004). *Method for the dihydroxylation of olefins using transition metal catalysts*, (U S Patent 6825377).
- Bellussi, G., Perego, C. Carati, A. Peratello, S. Previde, E. and Perego, G. (1994). in: Weitkamp, J. Karge, H.G. Pfeifer, H. Holderlich W. (Eds.). Zeolites and Related Microporous Materials: State of the Art. *Stud. Surf. Sci. Catal.*, Elsevier. 84: 85.
- Benitez, V. M. and Figoli, N. S. (2002). About the importance of surface W species in $\text{WO}_x/\text{Al}_2\text{O}_3$ during *n*-butene skeletal isomerization. *Catal. Commun.* 3(10): 487-492.
- Benitez, V. M., Querini, C. A. and Figoli, N. S. (2003). Characterization of $\text{WO}_x/\text{Al}_2\text{O}_3$ and $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalysts and their activity and deactivation during skeletal isomerization of 1-butene. *Appl. Catal. A: General* 252(2): 427-436.
- Blasco T., Corma A., Navarro, M. T. and Pariente, J. P. (1995). Synthesis, Characterization, and Catalytic Activity of Ti-MCM-41 Structures. *J. Catal.* 156: 65-74.

- Bobricheva, I. V., Stavitsky, I. A., Yermolaev, V. K., Kotsarenko, N. S., Shmachkova, V. P. and Kochubey, D. I. (1998). ESR study of paramagnetic sites in sulfated zirconia. *Catal. Lett.* 56(1): 23-27.
- Bonino, F., Damin, A., Bordiga, S., Lamberti, C. and Zecchina, A. (2003). Interaction of CD₃CN and Pyridine with the Ti(IV) Centers of TS-1 Catalysts: A Spectroscopic and Computational Study. *Langmuir* 19(6): 2155-2161.
- Bonino, F., Damin, A., Ricchiardi, G., Ricci, M., Spano, G., D'Aloisio, R., Zecchina, A., Lamberti, C., Prestipino, C. and Bordiga, S. (2004). Ti-Peroxo Species in the TS-1/H₂O₂/H₂O System. *J. Phys. Chem. B.* 108(11): 3573-3583.
- Bordiga, S., Damin, A., Bonino, F., Zecchina, A., Spano, G., Rivetti, F., Bolis, V., Prestipino, C. and Lamberti, C. (2002). Effect of Interaction with H₂O and NH₃ on the Vibrational, Electronic, and Energetic Peculiarities of Ti(IV) Centers TS-1 Catalysts: A Spectroscopic and Computational Study. *J. Phys. Chem. B.* 106(38): 9892-9905.
- Bosman, H. J. M., Pijpers, A. P. and Jaspers, A. W. M. A. (1996). An X-Ray Photoelectron Spectroscopy Study of the Acidity of SiO₂-ZrO₂ Mixed Oxides. *J. Catal.* 161(2): 551-559.
- Boyse, R. A. and Ko, E. I. (1997). Crystallization Behavior of Tungstate on Zirconia and Its Relationship to Acidic Properties. *J. Catal.* 171(1): 191-207.
- Braga, V. S., Dias, J. A., Dias, S. C. L. and de Macedo, J. L. (2005). Catalyst Materials Based on Nb₂O₅ Supported on SiO₂-Al₂O₃: Preparation and Structural Characterization. *Chem. Mater.* 17(3): 690-695.
- Brown, D. A., Khorlin, A. A., Lesiak, K. and Ren, W. Y. (2003). *Dermatological compositions and methods.* (U S Patent No. 6623724).
- Capel-Sanchez, M. C., Campos-Martin, J. M. and Fierro, J. L. G. (2003). Impregnation treatments of TS-1 catalysts and their relevance in alkene epoxidation with hydrogen peroxide. *Appl. Catal. A: General* 246(1): 69-77.
- Carlini, C., Giuttari, M., Galletti, A. M. R., Sbrana, G., Armaroli, T. and Busca, G. (1999). Selective saccharides dehydration to 5-hydroxymethyl-2-furaldehyde by heterogeneous niobium catalysts. *Appl. Catal. A: General* 183(2): 295-302.
- Carrazan, S. R. G., Martin, C., Solana, G. and Rives, V. (2001). A FT-IR Study of the Reactivity of Tungsta-Supported Catalysts toward Butan-2-ol. *Langmuir* 17(22): 6968-6973.

- Centi, G., Cavani, F. and Trifiro, F. (2001). Selective oxidation by heterogeneous catalysis. In Twigg, M. V. and Spencer, M. S. (eds). *Fundamental and applied catalysis*. 7. New York: Kluwer academic.
- Chaudhari, K., Srinivas, D. and Ratnasamy, P. (2001). Reactive Oxygen Species in Titanosilicates TS-1 and TiMCM-41: An In Situ EPR Spectroscopic Study. *J. Catal.* 203: 25-32.
- Chen, C. L., Cheng, S., Lin, H. P., Wong, S. T. and Mou, C. Y. (2001a). Sulfated zirconia catalyst supported on MCM-41 mesoporous molecular sieve. *Appl. Catal. A: General*. 215(1-2): 21-30.
- Chen, C. L., Tao, C., Soofin, L., Hong, P., Bhongale, C. J. and Mou, C. Y. (2001b). Direct impregnation method for preparing sulfated zirconia supported on mesoporous silica. *Microporous and Mesoporous Mater.* 50 (2-3): 201-208.
- Chen, L. Y., Chuah, G. K. and Jaenicke, S. (1998). Propylene epoxidation with hydrogen peroxide catalyzed by molecular sieves containing framework titanium. *J. Mol. Catal. A: Chemical* 132(2-3): 281-292.
- Clearfield, A., Serrette, G. P. D. and Khazi-Syed, A. H. (1994). Nature of hydrous zirconia and sulfated hydrous zirconia. *Catal Today* 20(2): 295-312.
- Clerici, M. G. and Ingallina, P. (1993). *Process for producing olefin oxides*. (US Patent No. 5,221,795).
- Clerici, M. G. and Ingallina, P. (1998). Oxidation reactions with in situ generated oxidants. *Catal. Today* 41: 351-364.
- Climent, M. J. Corma, A., Garcia, H., Guil-Lopez, R., Iborra, S. and Fornés, V. (2001). Acid-Base Bifunctional Catalysts for the Preparation of Fine Chemicals: Synthesis of Jasminaldehyde. *J. Catal.* 197(2): 385-393.
- Comelli, R. A., Vera, C. R. and Parera, J. M. (1995). Influence of ZrO₂ Crystalline Structure and Sulfate Ion Concentration on the Catalytic Activity of SO₄²⁻-ZrO₂. *J. Catal.* 151(1): 96-101.
- Corma, A. (1997). Solid acid catalysts. *Current Opinion in Solid State & Materials Science* 2: 63-75.
- Corma, A. and Garcia, H. (2003). Lewis Acids: From Conventional Homogeneous to Green Homogeneous and Heterogeneous Catalysis. *Chem. Rev.* 103(11): 4307-4366.

- Corma, A., Martínez, A. and Martínez, C. (1996). The effect of sulfation conditions and activation temperature of sulfate-doped ZrO₂, TiO₂ and SnO₂ catalysts during isobutane/2-butene alkylation. *Appl. Catal. A: General* 144(1-2): 249-268.
- Cundy, C. S. and Cox, P. A. (2003). The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chem. Rev.* 103: 663-701.
- da Silva, C. L. T., Camorim, V. L. L., Zotin, J. L., Pereira, M. L. R. D. and Faro Jr., A. C. (2000). Surface acidic properties of alumina-supported niobia prepared by chemical vapour deposition and hydrolysis of niobium pentachloride. *Catal. Today* 57(3-4): 209-217.
- Dalai, A. K., Sethuraman, R., Bakhshi, N. N., Idem, R. O. and Katikaneni, S. P. R. (2002). Performance Evaluation of Sulfated-TiO₂ as a Modifier to Co-Ni-ZrO₂ Catalyst in a Dual-Bed Reactor for the Selective Production of C₄ Hydrocarbons from Syngas. *Energy & Fuels* 16(1): 87-95.
- Damin, A., Bonino, F., Ricchiardi, G., Bordiga, S., Zecchina, A. and Lamberti, C. (2002). Effect of NH₃ Adsorption on the Structural and Vibrational Properties of TS-1. *J. Phys. Chem. B.* 106(30): 7524-7526.
- Damyanova, S., Grange, P. and Delmony, B. (1997). Surface Characterization of Zirconia-Coated Alumina and Silica Carriers. *J. Catal.* 168: 421-430.
- Damyanova, S., Dimitrov, L., Petrov, L. and Grange, P. (2003). Effect of niobium on the surface properties of Nb₂O₅-SiO₂-supported Mo catalysts. *Appl. Surface Science* 214(1-4): 68-74.
- Das, D., Mishra, H. K., Parida, K. M. and Dalai, A. K. (2002). Preparation, physico-chemical characterization and catalytic activity of sulphated ZrO₂-TiO₂ mixed oxides. *J. Mol. Catal. A: Chemical* 189(2): 271-282.
- Das, D., Mishra, H. K., Dalai, A. K. and Parida, K. M. (2003). Isopropylation of benzene over sulfated ZrO₂-TiO₂ mixed-oxide catalyst. *Appl. Catal. A: General* 243: 271-284.
- Davies, L. J., McMorn, P., Bethell, D., Page, P. C. B., King, F., Hancock, F. E. and Hutchings, G. J. (2001). Oxidation of crotyl alcohol using Ti-β and Ti-MCM-41 catalysts. *J. Mol. Catal. A: Chemical* 165: 243-247.
- Davis, B. H., Keogh, R. A. and Srinivasan, R. (1994). Sulfated zirconia as a hydrocarbon conversion catalyst. *Catal. Today* 20: 219-256.

- Davis, B. H., Keogh, R. A., Alerasool, S., Zalewski, D. J., Day, D. E. and Doolin, P. K. (1999). Infrared Study of Pyridine Adsorbed on Unpromoted and Promoted Sulfated Zirconia. *J. Catal.* 183(1): 45-52.
- Delahay, G., Ensueque, E., Coq, B. and Figuéras, F. (1998). Selective Catalytic Reduction of Nitric Oxide by *n*-Decane on Cu/Sulfated-Zirconia Catalysts in Oxygen Rich Atmosphere: Effect of Sulfur and Copper Contents. *J. Catal.* 175(1): 7-15.
- Dijs, I. J., Geus, J. W. and Jenneskens, L. W. (2003). Effect of Size and Extent of Sulfation of Bulk and Silica-Supported ZrO₂ on Catalytic Activity in Gas- and Liquid-Phase Reactions. *J. Phys. Chem. B.* 107: 13403-13413.
- Dong, L., Hu, Y., Xu, F., Lu, D., Xu, B., Hu, Z. and Chen, Y. (2000). A Study on the Surface Properties of Ceria-Supported Tungsten and Copper Oxides. *J. Phys. Chem. B.* 104(1): 78-85.
- Drago, R. S., Dias, S. C., McGilvray, J. M. and Mateus, A. L. M. L. (1998). Acidity and Hydrophobicity of TS-1. *J. Phys. Chem. B.* 102(9): 1508-1514.
- Ecornier, M. A., Wilson, K. and Lee, A. F. (2003). Structure–reactivity correlations in sulphated-zirconia catalysts for the isomerisation of α -pinene. *J. Catal.*, 215(1): 57-65.
- Eibl, S., Gates, B. C. and Knozinger, H. (2001). Structure of WO_x/TiO₂ Catalysts Prepared from Hydrous Titanium Oxide Hydroxide: Influence of Preparation Parameters. *Langmuir* 17(1): 107-115.
- Esposito, A., Taramasso, M. and Neri, C. (1983). *Hydroxylating aromatic hydrocarbons*. (US Patent No. 4,396,783).
- Flanigen, E. M. (1976). Structural analysis by infrared spectroscopy. In: Rabo, J. A. ed. Zeolite chemistry and catalysis. *ACS Monograph* 171: 80-117.
- Francisco, M. S. P., Landers, R. and Gushikem, Y. (2004b). Local order structure and surface acidity properties of a Nb₂O₅/SiO₂ mixed oxide prepared by the sol–gel processing method. *J. Solid State Chem.* 177: 2432–2439.
- Fu, X., Zeltner, W. A., Yang, Q. and Anderson, M. A. (1997). Catalytic Hydrolysis of Dichlorodifluoromethane (CFC-12) on Sol-Gel-Derived Titania Unmodified and Modified with H₂SO₄. *J. Catal.* 168(2): 482-490.
- Gallo, J. M. R., Paulino, I. S. and Schuchardt, U. (2004). Cyclooctene epoxidation using Nb-MCM-41 and Ti-MCM-41 synthesized at room temperature. *Appl. Catal. A: General* 266(2): 223-227.

- Gang, L., Xinwen, G., Sheng, W. X., Qi, Z., Xinhe, B., Xiuwen, H. and Liwu, L. (1999). Synthesis of titanium silicalites in different template systems and their catalytic performance. *Appl. Catal. A: General* 185: 11-18.
- Gao, H., Lu, W. and Chen, Q. (2000). Characterization of titanium silicalite-1 prepared from aqueous $TiCl_3$. *Microporous and Mesoporous Mater.* 34: 307-315.
- Gao, X., Wachs, I. E., Wong, M. S. and Ying, J. Y. (2001). Structural and Reactivity Properties of Nb-MCM-41: Comparison with That of Highly Dispersed Nb_2O_5/SiO_2 Catalysts. *J. Catal.* 203(1): 18-24.
- Gao, Z. and Xia, Q. H. (1997). Crystallization kinetics of pure TS-1 zeolite using quaternary ammonium halides as templates. *Mater. Chem. and Physics* 47(2-3): 225-230.
- Gervasini, A. (1999). Characterization of the textural properties of metal loaded ZSM-5 zeolites. *Appl. Catal. A: General* 180(1-2): 71-82.
- Gontier, S. and Tuel, A. (1996). Synthesis of titanium silicalite-1 using amorphous SiO_2 as silicon source. *Zeolites* 16: 184-195.
- Grieken, R., Serrano, D. P., Melero, J. A. and García, A. (2004). Effect of the solvent in the liquid phase rearrangement of 1,2-epoxyoctane over Al-MCM-41 and Al-TS-1 catalysts. *J. Mol. Catal. A: Chemical* 222(1-2): 167-174.
- Gusev, V. (1998). Molecule of the month, MCM-41. <http://www.bris.ac.uk/Depts/Chemistry/MOTM/mcm41/mcm41.htm>
- Gushikem, Y. and Rosatto, S. S. (2001). Metal Oxide Thin Films Grafted on Silica Gel Surfaces: Recent Advances on the Analytical Application of these Materials. *J. Braz. Chem. Soc.* 12(6): 695-705.
- Gutiérrez-Alejandre, A., Castillo, P., Ramírez, J., Ramis, G. and Busca, G. (2001). Redox and acid reactivity of wolframyl centers on oxide carriers: Brønsted, Lewis and redox sites. *Appl. Catal. A: General* 216: 181-194.
- Guyon, M., Le Chanu, V., Gilot, P., Kessler, H. and Prado, G. (1996). Experimental study of the formation and the reaction of an intermediate during the lean NO_x reaction over Cu-ZSM-5. *Appl. Catal. B: Environmental* 8(2): 183-196.
- Habuta, Y., Narishige, N., Okumura, K., Katada, N. and Niwa, M. (2003) Catalytic activity and solid acidity of vanadium oxide thin layer loaded on TiO_2 , ZrO_2 , and SnO_2 . *Catal. Today* 78(1-4): 131-138.

- Han, J. and Kumacheva, E. (2001). Monodispersed Silica-Titanyl Sulfate Microspheres. *Langmuir* 17(25): 7912-7917.
- Hanaoka, T., Takeuchi, K., Matsuzaki, T. and Sugi, Y. (1990). Niobic acid as solid acid catalyst for ring-opening reaction of phenyloxirane. *Catal. Today* 8(1): 123-132.
- Hartmuth C. Kolb, Michael S. VanNieuwenhze, K. Barry Sharpless 1994. Catalytic Asymmetric Dihydroxylation. *Chem. Rev.* 94(8): 2483-2547.
- Henry, P. F., Weller, M. T. and Wilson, C. C. (2001). Structural Investigation of TS-1: Determination of the True Nonrandom Titanium Framework Substitution and Silicon Vacancy Distribution from Powder Neutron Diffraction Studies Using Isotopes. *J. Phys. Chem. B.* 105: 7452-7458.
- Hess, A. and Kemnitz, E. (1997). Surface acidity and catalytic behavior of modified zirconium and titanium dioxides. *Appl. Catal. A: General* 149(2): 373-389.
- Higgins, J. B., LaPierre, R. B., Schlenker, J. L., Rohrman, A. C., Wood, J. D., Kerr, G. T. and Rohrbaugh, W. J. (1988). The framework topology of zeolite beta. *Zeolites* 8: 446-452.
- Hijar, C. A., Jacubinas, R. M., Eckert, J., Henson, N. J., Hay, P. J. and Ott, K. C. (2000). The Siting of Ti in TS-1 Is Non-Random. Powder Neutron Diffraction Studies and Theoretical Calculations of TS-1 and FeS-1. *J. Phys. Chem. B.* 104(51): 12157-12164.
- Hino, M., Kobayashi, S. and Arata, K. (1979). Solid catalyst treated with anion. 2. Reactions of butane and isobutane catalyzed by zirconium oxide treated with sulfate ion. Solid superacid catalyst. *J. Am. Chem. Soc.* 101: 6439-6441.
- Hoelderich W. F. (2000a). 'One-pot' reactions: a contribution to environmental protection. *Appl. Catal. A: General* 194 –195: 487–496.
- Hoelderich W. F. (2000b). Environmentally benign manufacturing of fine and intermediate chemicals. *Catal. Today* 62(1): 115-130
- Hollstein, E. J., Wei; J. T. and Hsu, C. Y. (1990). *Catalyst for hydrocarbon conversion and conversion process utilizing the same.* (U. S. Patent 4,918,041).
- Hsu, C. Y., Patel, V. K., Vahlsing, D. H., Wei, J. T. and Myers, Jr., H. K. (1991). *Liquid phase isomerization of alkanes.* (U. S. Patent 5,019,671).
- Hu, S., Willey, R. J. and Notari, B. (2003). An investigation on the catalytic properties of titania–silica materials. *J. Catal.* 220: 240–248.

- Huang, Y. Zhao, B. and Xie, Y. (1998). A novel way to prepare silica supported sulfated titania. *Appl. Catal. A: General* 171: 65-73.
- Huang, Y. Y., Zhao, B. Y. and Xie, Y. C. (1998). A new method to prepare silica- or alumina-supported sulfated zirconia. *Appl. Catal. A: General* 173: 27-35.
- Ichikuni, N. Shirai, M. and Iwasawa, Y. (1996). Surface structures and catalytic properties of supported niobium oxides. *Catal. Today* 28(1-2): 49-58.
- Iglesia, E., Barton, D. G., Biscardi, J. A., Gines, M. J. L. and Soled, S. L. (1997). Bifunctional pathways in catalysis by solid acids and bases. *Catal. Today* 38(3): 339-360.
- Iizuka, T., Fujie, S., Ushikubo, T., Chen, Z. and Tanabe, K. (1986). Esterification of acrylic acid with methanol over niobic acid catalyst. *Appl. Catal.* 28: 1-5.
- Jehng, J. M. and Wachs, I. E. (1990). The molecular structures and reactivity of supported niobium oxide catalysts. *Catal. Today* 8(1): 37-55.
- Jehng, J. M. and Wachs, I. E. (1991). Molecular structures of supported niobium oxide catalysts under ambient conditions. *J. Mol. Catal.* 67(3): 369-387.
- Jehng, J. M. and Wachs, I. E. (1993). Molecular design of supported niobium oxide catalysts. *Catal. Today* 16(3-4): 417-426.
- Jehng, J. -M., Hu, H., Gao, X. and Wachs, I. E. (1996). The dynamic states of silica-supported metal oxide catalysts during methanol oxidation. *Catal. Today* 28(4): 335-350.
- Jiang, D. Zhao, B. Xie, Y. Pan, G. Ran, G. and Min, E. (2001). Structure and basicity of γ -Al₂O₃-supported MgO and its application to mercaptan oxidation. *Appl. Catal. A: General* 219(1-2): 69-78.
- Jiang, X. Z., Zhang, L. Q., Wu, X. H. and Zheng, Lei. (1996). Catalytic decomposition of methylene chloride by sulfated oxide catalysts. *Appl. Catal. B: Environmental* 9(1-4): 229-237.
- Jorda, E., Tuel, A., Teissier, R. and Kervennal, J. (1997). TiF₄: An original and very interesting precursor to the synthesis of titanium containing silicalite-1. *Zeolites* 19: 238-245.
- Jung, S. M., Dupont, O. and Grange, P. (2001). TiO₂-SiO₂ mixed oxide modified with H₂SO₄: I. Characterization of the microstructure of metal oxide and sulfate. *Appl. Catal. A: General* 208(1-2): 393-401.

- Jung, S. M. and Grange, P. (2000). Characterization and reactivity of pure TiO_2 – SO_4^{2-} SCR catalyst: influence of SO_4^{2-} content. *Catal. Today* 59(3-4): 305-312.
- Karakonstantis, L., Bourikas, K. and Lycourghiotis, A. (1996). Tungsten–Oxo-Species Deposited on Alumina. I. Investigation of the Nature of the Tungstates Deposited on the Interface of the γ -Alumina/Electrolyte Solutions at Various pH's. *J. Catal.* 162(2): 295-305.
- Katada, N., Fujii, T., Iwata, K., Hibino, Y. and Niwa, M. (1999). Concentration of Hydroxyl Groups on Silica Monolayer Solid Acid Catalyst. *J. Catal.*, 186(2): 478-480.
- Katz, A. (1999). The synthesis and characterization of molecularly imprinted materials. PhD Thesis. California Institute of Technology. California.
- Kelly-Rowley, A. M. and Chatterjee, A. K. (2004). *Branched alcohols and diols for increased dot size and reliability.* (U S Patent 6808556).
- Khomane, R. B., Kulkarni, B. D., Paraskar, A. and Sainkar, S. R. (2002). Synthesis, characterization and catalytic performance of titanium silicalite-1 prepared in micellar media. *Mater. Chem. and Physics* 76: 99-103.
- Kijenski, J., Winiarek, P., Paryjczak, T., Lewicki, A. and Mikolajska, A. (2002) Platinum deposited on monolayer supports in selective hydrogenation of furfural to furfuryl alcohol. *Appl. Catal. A: General* 233(1-2): 171-182.
- Kilos, B., Aouine, M., Nowak, I., Ziolk, M. and Volta, J. C. (2004). The role of niobium in the gas- and liquid-phase oxidation on metallosilicate MCM-41-type materials. *J. Catal.* 224(2): 314-325.
- Klimenkov, M., Nepijko, S. A. Matz, W. and Bao, X. (2001). The study of Ti doped ZSM-5 particles and cavities inside them. *J. Crystal Growth* 231: 577–588.
- Ko, E. I. and Weissman, J. G. (1990). Structures of niobium pentoxide and their implication on chemical behavior. *Catal. Today* 8: 27-36.
- Kresge, C. T., Leonowicz, M. E., Roth, W. J. and Vartuli, J. C. (1993). *Use of amphiphilic compounds to produce novel classes of crystalline oxide materials.* (U.S. Patent No. 5,250,282).
- Krijnen, S., Sánchez, P., Jakobs, B. T. F. and van Hooff, J. H. C. A. (1999). controlled post-synthesis route to well-defined and active titanium Beta epoxidation catalysts. *Microporous and Mesoporous Mater.* 31: 163-173.

- Kung, H. H. (1989). Transition metal oxides: surface chemistry and catalysis. *Stud. Surf. Science and Catal.* 45.
- Lapisardi, G., Chiker, F., Launay, F., Nogier, J. P. and Bonardet, J. L. (2004). A "one-pot" synthesis of adipic acid from cyclohexene under mild conditions with new bifunctional Ti-ALSBA mesostructured catalysts. *Catal. Commun.*, 5(6): 277-281.
- Lapisardi, G., Chiker, F., Launay, F., Nogier, J. P. and Bonardet, J. L. (2005). Preparation, characterisation and catalytic activity of new bifunctional Ti-ALSBA15 materials. Application to a "one-pot" green synthesis of adipic acid from cyclohexene and organic hydroperoxides. *Microporous Mesoporous Mater.*, 78(2-3): 289-295.
- Lau, C., Brück, S., Mai, H. -J. and Kynast, U. (2001). Incorporation of tungsten trioxide into faujasites and sodalites by solid-state reactions. *Microporous and Mesoporous Mater.* 47: 339-344.
- Lei, T., Xu, J. S., Tang, Y., Hua, W. M. and Gao, Z. (2000). New solid superacid catalysts for *n*-butane isomerization: γ -Al₂O₃ or SiO₂ supported sulfated zirconia. *Appl. Catal. A: General.* 192: 181-188.
- Li, M., Feng, Z., Xiong, G., Ying, P., Xin, Q., and Li, C. (2001). Phase transformation in the surface region of zirconia detected by UV raman spectroscopy. *J. Phys. Chem. B.* 105: 8107-8111.
- Lin, W. and Frei, H. (2002). Photochemical and FT-IR Probing of the Active Site of Hydrogen Peroxide in Ti Silicalite Sieve. *J. Am. Chem. Soc.* 124(31): 9292-9298.
- Liu, S., Wang, L., Ohnishi, R. and Ichikawa, M. (1999). Bifunctional Catalysis of Mo/HZSM-5 in the Dehydroaromatization of Methane to Benzene and Naphthalene XAFS/TG/DTA/MASS/FTIR Characterization and Supporting Effects. *J. Catal.* 181(2): 175-188.
- Logie, V., Maire, G., Michel, D. and Vignes, J. -L. (1999). Skeletal Isomerization of Hexenes on Tungsten Oxide Supported on Porous γ -Alumina. *J. Catal.* 188(1): 90-101.
- Lónyi, F. and Valyon, J. (2001). On the interpretation of the NH₃-TPD patterns of H-ZSM-5 and H-mordenite. *Microporous and Mesoporous Mater.* 47(2-3): 293-301.

- Lónyi, F., Valyon, J., Engelhardt, J., and Mizukami, F. (1996). Characterization and Catalytic Properties of Sulfated $\text{ZrO}_2\text{-TiO}_2$ Mixed Oxides. *J. Catal.* 160: 279-289.
- Lu, G. (1995). Catalytic properties of $\text{SO}_4^{2-}/\text{Ti-M-O}$ superacids in esterification. *Appl. Catal. A: General* 133(1): 11-18.
- Luan, Z., Maes, E. M., van der Heide, P. A. W., Zhao, D., Czernuszewicz, R. S. and Kevan, L. (1999). Incorporation of Titanium into Mesoporous Silica Molecular Sieve SBA-15. *Chem. Mater.* 11: 3680-3686.
- Lucas, A., Valverde, J. L., Cañizares, P. and Rodriguez, L. (1998). Partial oxidation of methane to formaldehyde over W/HZSM-5 catalysts. *Appl. Catal. A: General* 172(1): 165-176.
- Lucas, A., Valverde, J. L., Rodriguez, L., Sanchez, P. and Garcia, M. T. (2001). Modified W/HZSM-5 catalysts: structure and catalytic properties *Appl. Catal. A: General* 171(1-2): 195-203.
- Ma, Z., Yue, Y., Deng, X. and Gao, Z. (2002). Nanosized anatase TiO_2 as precursor for preparation of sulfated titania catalysts. *J. Mol. Catal. A: Chemical* 178(1-2): 97-104.
- Macht, J., Baertsch, C. D., May-Lozano, M., Soled, S. L., Wang, Y. and Iglesia, E. (2004). Support effects on Brønsted acid site densities and alcohol dehydration turnover rates on tungsten oxide domains. *J. Catal.* 227(2): 479-491.
- Mamede, A. S., Payen, E., Grange, P., Poncelet, G., Ion, A., Alifanti, M. and Pârvulescu, V. I. (2004). Characterization of WO_x/CeO_2 catalysts and their reactivity in the isomerization of hexane. *J. Catal.* 223(1): 1-12.
- Martin, C., Malet, P., Solana, G. and Rives, V. (1998). Structural Analysis of Silica-Supported Tungstates. *J. Phys. Chem. B.* 102(15): 2759-2768.
- Meijers, S., Gielgens, L., and Ponc, V. (1995). IR Spectroscopic Study of the Skeletal Isomerization of Butene by Alumina-Supported Tungsten Oxide Catalysts. *J. Catal.* 156(1): 147-153
- Mendes, F. M. T., Perez, C. A., Soares, R. R., Noronha, F. B. and Schmal, M. (2003). Ammonium complex of niobium as a precursor for the preparation of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts. *Catal. Today* 78: 449-458.
- Milbradt, R., Klein, S., Scherl, F. X., Gatter, E. and Oberhauser, A. (2005). *Cosmetic formulations of having high aqueous solubility and low flash points.* (U S Patent 6881399).

- Mitsutani, A. (2002). Future possibilities of recently commercialized acid/base-catalyzed chemical processes. *Catal. Today* 73: 57-63.
- Morais, M., Torres, E. F., Carmo, L. M. P. M., Pastura, N. M. R., Gonzalez, W. A., dos Santos, A. C. B. and Lachter, E. R. (1996). Benzylolation of toluene and anisole by benzyl alcohol catalysed by niobic acid. *Catal. Today* 28(1-2): 17-21.
- Morterra, C., Cerrato, G. and Bolis, V. (1993). Lewis and Brønsted acidity at the surface of sulfate-doped ZrO₂ catalysts. *Catal. Today*. 17: 505-515.
- Morterra, C., Cerrato, G., Di Ciero, S., Signoretto, M., Pinna, F. and Strukul, G. (1997). Platinum-Promoted and Unpromoted Sulfated Zirconia Catalysts Prepared by a One-Step Aerogel Procedure: 1. Physico-chemical and Morphological Characterization. *J. Catal.* 165(2): 172-183.
- Munakata, H., Oumi, Y. and Miyamoto, A. (2001). A DFT Study on Peroxo-Complex in Titanosilicate Catalyst: Hydrogen Peroxide Activation on Titanosilicalite-1 Catalyst and Reaction Mechanisms for Catalytic Olefin Epoxidation and for Hydroxylamine Formation from Ammonia. *J. Phys. Chem. B*. 105(17): 3493-3501.
- Neylon, M. K., Castagnola, M. J., Castagnola, N. B. and Marshall, C. L. (2004). Coated bifunctional catalysts for NO_x SCR with C₃H₆: Part I: water-enhanced activity. *Catal. Today* 96(1-2): 53-60.
- Nicholas, C. P. and Marks, T. J. (2004). Zirconium Hydrocarbyl Chemisorption on Sulfated Metal Oxides: New Supports, Chemisorption Pathways, and Implications for Catalysis. *Langmuir* 20(22): 9456-9462.
- Niederer, J. P. M. and Hölderich, W. F. (2002). Oxidation capabilities of BEA isomorphously substituted with molybdenum, vanadium and titanium: an explorative study. *Appl. Catal. A: General* 229 51-64.
- Niwa, M. and Igarashi, J. (1999). Role of the solid acidity on the MoO₃ loaded on SnO₂ in the methanol oxidation into formaldehyde. *Catal. Today* 52(1): 71-81.
- Niwa, M. Habuta, Y. Okumura, K. and Katada, N. (2003). Solid acidity of metal oxide monolayer and its role in catalytic reactions. *Catal. Today* 87(1-4): 213-218.

- Noda, L. K., de Almeida, R. M., Gonçalves, N. S., Probst, L. F. D. and Sala, O. (2003). TiO₂ with a high sulfate content - thermogravimetric analysis, determination of acid sites by infrared spectroscopy and catalytic activity. *Catal. Today* 85: 69–74.
- Noronha, F. B., Frydman, A., Aranda, D. A. G., Perez, C., Soares, R. R., Morawek, B., Castner, D., Campbell, C. T., Frety, R. and Schmal, M. (1996). The promoting effect of noble metal addition on niobia-supported cobalt catalysts. *Catal. Today* 28(1-2): 147-157.
- Nowak, I. and Ziolk, M. (1999). Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis. *Chem. Rev.* 99: 3603-3624.
- Nowak, I. and Ziolk, M. (2005). Effect of texture and structure on the catalytic activity of mesoporous niobosilicates for the oxidation of cyclohexene. *Microporous and Mesoporous Mater.* 78(2-3): 281-288.
- Nowak, I., Kilos, B., Ziolk, M. and Lewandowska, A. (2003). Epoxidation of cyclohexene on Nb-containing meso- and macroporous materials. *Catal. Today* 78(1-4): 487-498.
- Okazaki, S. Iizuka T. and Kado. S. (1987). *Solid acid catalyst of acid-treated hydrated niobium oxide and method for its preparation*. (U. S. Patents No. 4,652,544).
- Okuhara, T. (2002). Water-Tolerant Solid Acid Catalysts. *Chem. Rev.* 102(10): 3641-3666.
- Onfroy, T., Clet, G. and Houalla, M. (2005). Acidity, Surface Structure, and Catalytic Performance of WO_x Supported on Monoclinic Zirconia. *J. Phys. Chem. B.* in press.
- Ozin, G. A. and Ozkar, S. (1990). Intrazeolite metal carbonyl phototopotaxy: from tungsten(VI) oxide quantum dots to a zero-dimensional semiconductor quantum supralattice. *J. Phys. Chem.* 94(19): 7556-7561.
- Paulis, M., Martín, M., Soria, D. B., Díaz, A., Odriozola J. A. and Montes, M. (1999). Preparation and characterization of niobium oxide for the catalytic aldol condensation of acetone. *Appl. Catal. A: General* 180(1-2): 411-420.
- Parvulescu, V., Coman, S., Grange, P. and Parvulescu, V. I. (1999). Preparation and characterization of sulfated zirconia catalysts obtained via various procedures. *Appl. Catal. A: General* 176: 27-43.

- Paze, C., Civalleri, B., Bordiga, S. and Zecchina, A. (1998). HCl and HCl-Base Adducts in Silicalite Channels as Models of Acid-Base Interactions in Zeolites: An IR and Theoretical Study. *J. Phys. Chem. B.* 102(52): 10753-10764.
- Perego, C., Carati, A., Ingallina, P., Mantegazza, M.A. and Bellussi, G. (2001) Production of titanium containing molecular sieves and their application in catalysis. *Appl. Catal. A: General* 221(1-2): 63-72.
- Pereira, E. B., Pereira, M. M., Lam, Y.L., Perez, C. A.C. and Schmal. M. (2000). Synthesis and characterization of niobium oxide layers on silica and the interaction with nickel. *Appl. Catal. A: General* 197: 99–106.
- Platero, E. E., Mentrui, M. P., Areán, C. O. and Zecchina, A. (1996). FTIR Studies on the Acidity of Sulfated Zirconia Prepared by Thermolysis of Zirconium Sulfate. *J. Catal.* 162: 268-276.
- Pohl, G. and Gaube, H. (1985). In *Ullmann's Encyclopedia of Industrial Chemistry*; VCH: Weinheim,; Vol. A1, p 305-320.
- Prasad, M. R., Kamalakar, G., Kulkarni, S. J., Raghavan, K. V., Narasimha Rao, K., Sai Prasad, P. S. and Madhavendra, S. S. (2002). An improved process for the synthesis of titanium-rich titanium silicates (TS-1) under microwave irradiation. *Catal. Commun.* 3: 399-404.
- Raja, R., Sankar, G. and Thomas, J. M. (2001). Bifunctional Molecular Sieve Catalysts for the Benign Ammoximation of Cyclohexanone: One-Step, Solvent-Free Production of Oxime and Caprolactam with a Mixture of Air and Ammonia. *J. Am. Chem. Soc. (Commun.)* 123(33): 8153-8154.
- Rakshe, B., Ramaswamy, V., Hegde, S. G., Vetrivel, R. and Ramaswamy, A. V. (1997). Crystalline, microporous zirconium silicates with MFI structure. *Catal. Lett.* 45: 41-50.
- Ramírez, J. and Alejandre, A. G. (1997). Characterization and Hydrodesulfurization Activity of W-Based Catalysts Supported on Al₂O₃-TiO₂ Mixed Oxides. *J. Catal.* 170(1): 108-122.
- Reddy, B. M., Sreekanth, P. M., Yamada, Y., Xu, Q. and Kobayashi, T. (2002). Surface characterization of sulfate, molybdate, and tungstate promoted TiO₂-ZrO₂ solid acid catalysts by XPS and other techniques. *Appl. Catal. A: General* 228(1-2): 269-278.
- Reiche, M. A., Maciejewski, M. and Baiker, A. (2000). Characterization by temperature programmed reduction. *Catal. Today*, 56(4): 347-355.

- Resini, C. Panizza, M. Raccoli, F. Fadda, M. Carnasciali, M. M. Busca, G. Lopez E. F. and Escribano, V. S. (2003). Oxidation of ethane and cyclohexane over vanadia-niobia-silica catalysts. *Appl. Catal. A: General* 251(1): 29-38.
- Ricchiardi, G., Damin, A., Bordiga, S., Lamberti, C., Spano, G., Rivetti, F. and Zecchina, A. (2001). Vibrational Structure of Titanium Silicate Catalysts. A Spectroscopic and Theoretical Study. *J. Am. Chem. Soc.* 123(46): 11409-11419.
- Rosenberg, D. J., Bachiller-Baeza, B., Dines, T. J. and Anderson, J. A. (2003). Nature of Surface Sulfate Species and the Generation of Active Sites on Silica-Zirconia Mixed-Oxide Catalysts. *J. Phys. Chem. B.* 107: 6526-6534.
- Samantaray, S. K., Mishra, T. and Parida, K. M. (2000). Studies on anion promoted Titania: 2: Preparation, characterisation and catalytic activity towards aromatic alkylation over sulfated titania. *J. Mol. Catal. A: Chemical* 156(1-2): 267-274.
- Samantaray, S. K., Mohapatra, P. and Parida, K. M. (2003). Physico-chemical characterisation and photocatalytic activity of nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ towards degradation of 4-nitrophenol. *J. Mol. Catal. A: Chemical* 198(1-2): 277-287.
- Sankar, G., Thomas, J. M., Catlow, C. R. A., Barker, C. M., Gleeson, D. and Kaltsoyannis, N. (2001). The Three-Dimensional Structure of the Titanium-Centered Active Site during Steady-State Catalytic Epoxidation of Alkenes. *J. Phys. Chem. B.* 105(38): 9028-9030.
- Santiesteban, J. R., Vartuli, J. C., Han, S., Bastian, R. D. and Chang, C. D. (1997). Influence of the Preparative Method on the Activity of Highly Acidic WO_x/ZrO_2 and the Relative Acid Activity Compared with Zeolites. *J. Catal.* 168: 431-441.
- Sasidharan, M., Wu, P. and Tatsumi, T. (2002). Direct Formation of Pinacols from Olefins over Various Titano-Silicates, *J. Catal.* 209: 260-265.
- Saxton, R. J., Zajacek, J. G. and Crocco, G. L. (1997). *Titanium containing molecular sieve having a zeolite beta structure.* (U. S. Patent No. 5,695,736).
- Scheithauer, M., Cheung, T. K., Jentoft, R. E., Grasselli, R. K., Gates, B. C. and Knozinger, H. (1998). Characterization of WO_x/ZrO_2 by Vibrational Spectroscopy and *n*-Pentane Isomerization Catalysis. *J. Catal.* 180(1): 1-13.
- Scheithauer, M., Grasselli, R. K. and Knozinger, H. (1998). Genesis and Structure of WO_x/ZrO_2 Solid Acid Catalysts. *Langmuir* 14(11): 3019-3029.

- Sever, R. R. and Root, T. W. (2003). DFT Study of Solvent Coordination Effects on Titanium-Based Epoxidation Catalysts. Part One: Formation of the Titanium Hydroperoxo Intermediate. *J. Phys. Chem. B.* 107(17): 4080-4089.
- Shen, M., Hu, Y., Zhu, H., Liu, T., Wei, S., Dong, L. and Chen, Y. (2003). A study of thoria on the surface of γ -Al₂O₃. *J. Colloid and Interface Science* 257(2): 408-41.
- Sheldon, R. A. (1980). Synthetic and mechanistic aspects of metal-catalysed epoxidations with hydroperoxides. *J. Mol. Catal.* 7: 107-126.
- Sheldon, R. A. and Dakka, J. (1994). Heterogeneous catalytic oxidations in the manufacture of fine chemicals. *Catal. Today* 19: 215-245.
- Shetti, V. N., Manikandan, P., Srinivas, D. and Ratnasamy, P. (2003). Reactive oxygen species in epoxidation reactions over titanosilicate molecular sieves. *J. Catal.* 216(1-2): 461-467.
- Shibata, M. and Gabelica, Z. (1997). Alkali-free synthesis of MFI type borotitanosilicates using methylamine. *Microporous Mater.*, 11(5-6): 237-245.
- Shirai, M., Ichikuni, N., Asakura, K. and Iwasawa, Y. (1990). Preparation and catalytic properties of single, pair, and monolayer niobium catalysts. *Catal Today* 8: 57-66.
- Smirnov, K. S. and van de Graaf, B. (1996). On the origin of the band at 960 cm⁻¹ in the vibrational spectra of Ti-substituted zeolites. *Microporous Mater.* 7: 133-138.
- Sohn, J. R. and Park, M. Y. (1998). Characterization of Zirconia-Supported Tungsten Oxide Catalyst. *Langmuir* 14: 6140-6145.
- Sohn, J. R. and Park, M. Y. (2003). The roles of active sites of nickel sulfate supported on γ -Al₂O₃ for ethylene dimerization. *Appl. Catal. A: General* 239(1-2): 269-278
- Sohn, J. R. and Seo, D. H. (2003). Preparation of new solid superacid catalyst, zirconium sulfate supported on γ -alumina and activity for acid catalysis. *Catal. Today* 87: 219-226.
- Srinivas, D., Manikandan, P., Laha, S. C., Kumar, R. and Ratnasamy, P. (2003) Reactive oxo-titanium species in titanosilicate molecular sieves: EPR investigations and structure–activity correlations. *J. Catal.* 217: 160–171.

- Srinivasan, R., Keogh, R. A., Milburn, D. R. and Davis B. H. (1995). Sulfated Zirconia Catalysts: Characterization by TGA/DTA Mass Spectrometry. *J. Catal.* 153(1): 123-130.
- Su, C., Li, J., He, D., Cheng, Z. and Zhu, Q. (2000). Synthesis of isobutene from synthesis gas over nanosize zirconia catalyst. *Appl. Catal. A: General* 202: 81-89.
- Szmant, H. H. (1989). *Organic Building Blocks of the Chemical Industry*. Wiley: New York. p 347.
- Tanabe K. (1990). Application of niobium oxides as catalysts. *Catal. Today*. 8(1): 1-11.
- Tanabe K. (2002). Catalytic application of niobium compounds. *Catal. Today*. 2813: 1-13.
- Tanabe, K. (2003). Catalytic application of niobium compounds. *Catal. Today* 78: 65-77.
- Tanabe, K. and Okazaki, S. (1995). Various reactions catalyzed by niobium compounds and materials. *Appl. Catal. A: General* 133: 191-218.
- Tanabe K. and Hölderich, W. F. (1999). Industrial application of solid acid-base catalysts. *Appl. Catal. A: General*. 181: 399-434.
- Tanaka, T., Yoshida, T., Yoshida, H., Aritani, H., Funabiki, T. and Satohiro. (1996). XAFS study of niobium oxide on alumina. *Catal. Today* 28(1-2): 71-78
- Taramasso, M., Perego, G. and Notari, B. (1983). *Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides*. (U. S. Patents No. 4,410,501).
- Thangaraj, A., Kumar, R. and Sivasanker, S. (1992). Evidence for the simultaneous incorporation of Al and Ti in MFI structure (Al-TS-1). *Zeolites* 12(2): 135-137.
- Thomas, R. and Moulijn, J. A. (1982). A comparative study of γ -alumina supported molybdenum and tungsten oxide: relation between metathesis activity and reducibility. *J. Mol. Catal.* 15(1-2): 157-172.
- Tonti, S., Roffia, and P. Gervasutti, V. (1993). *Multistep process for the liquid phase ammoxidation of carbonyl compounds*. (US Patent No. 5,227,525).
- Tozzola, G., Mantegazza, M. A., Ranghino, G., Petrini, G., Bordiga, S., Ricchiardi, G., Lamberti, C., Zulian, R. and Zecchina, A. (1998). On the Structure of the Active Site of Ti-Silicalite in Reactions with Hydrogen Peroxide: A Vibrational and Computational Study. *J. Catal.* 179(1): 64-71.

- Tran, M. T., Gnep, N. S., Szabo, G. and Guisnet, M. (1998), Influence of the calcination temperature on the acidic and catalytic properties of sulphated zirconia. *Appl. Catal. A: General* 171: 207-217.
- Treacy, M. M. J., Higgins, J. B. and von Ballmoos, R. (1996). Collection of simulated XRD powder patterns for zeolites. 3rd. ed. Amsterdam: Elsevier.
- Trong On, D., Kaliaguine, S. and Bonneviot, L. (1995). Titanium Boralites with MFI Structure Characterized Using XRD, XANES, IR, and UV-Visible Techniques: Effect of Hydrogen Peroxide on the Preparation. *J. Catal.*, 157(1): 235-243
- Trong On, D., Nguyen, S. V., Hulea, V., Dumitriu, E. and Kaliaguine, S. (2003) Mono- and bifunctional MFI, BEA and MCM-41 titanium-molecular sieves. Part 1. Synthesis and characterization. *Microporous and Mesoporous Mater.* 57: 169–180.
- Tsipis, A. C. and Tsipis, C. A. (2000). Molecular Transition Metal Oxides: Ab Initio and Density Functional Electronic Structure Study of Tungsten Oxide Clusters. *J. Phys. Chem. A.* 104(4): 859-865.
- Tuel, A. and Taarit, Y. B. (1993). Synthesis of TS-1 from titanosilicate gels containing TPAOH/TEAOH and TPAOH/NH₄OH mixtures. *Microporous Mater.* 1: 179-189.
- Tuel, A. and Taarit, Y. B. (1994). Influence of the nature of silicon and titanium alkoxides on the incorporation of titanium in TS-1. *Appl. Catal. A: General.* 110: 137-151.
- Uguina, M. A., Serrano, D. P., Ovejero, G., van Grieken, R. and Camacho, M. (1995). Preparation of TS-1 by wetness impregnation of amorphous SiO₂-TiO₂ solids: influence of the synthesis variables. *Appl. Catal. A: General.* 124: 391-408.
- Uguina, M. A., Serrano, D. P., Sanz, R., Fierro, J. L. G., López-Granados, M. and Mariscal, R. (2000). Preliminary study on the TS-1 deactivation during styrene oxidation with H₂O₂. *Catal. Today* 61(1-4): 263-270.
- van der Pol, A. J. H. P. and van Hooff, J. H. C. (1992). Parameters affecting the synthesis of titanium silicalite 1. *Appl. Catal. A: General* 92(2): 93-111.
- van der Waal, J. C. and van Bekkum, H. (1997). Zeolite titanium beta: A versatile epoxidation catalyst. Solvent effects. *J. Mol. Catal. A: Chemical.* 124: 137-146.

- van der Waal, J. C., Kooyman, P. J., Jansen, J. C. and van Bekkum, H. (1998). Synthesis and characterization of aluminum-free zeolite titanium beta using di(cyclohexylmethyl) dimethylammonium as a new and selective template. *Microporous and Mesoporous Mater.* 25(1-3): 43-57.
- van der Waal, J. C., Rigutto, M. S. and van Bekkum, H. (1998). Zeolite titanium beta as a selective catalyst in the epoxidation of bulky alkenes. *Appl. Catal. A: General* 167: 331-342.
- Vayssilov, G. N. and van Santen, R. A. (1998). Catalytic Activity of Titanium Silicalites - a DFT Study. *J. Catal.* 175(2): 170-174.
- Védrine, J. C. Coudurier, G. Ouqour, A. Pries de Oliveira, P. G. and Volta J. C. (1996). Niobium oxide based materials as catalysts for acidic and partial oxidation type reactions. *Catal. Today* 28(1-2): 3-15.
- Vera, C. R., Pieck, C. L., Shimizu, K. and Parera, J. M. (2002). Tetragonal structure, anionic vacancies and catalytic activity of SO_4^{2-} - ZrO_2 catalysts for *n*-butane isomerization. *Appl. Catal. A: General* 230: 137-151.
- Wachs, I. E., Jehng, J. -M., Deo, G., Hu, H. and Arora, N. (1996). Redox properties of niobium oxide catalysts. *Catal. Today* 28(1-2): 199-205.
- Wang, X., Chen, H-Y. and Sachtler, W. M. H. (2000). Catalytic reduction of NO_x by hydrocarbons over Co/ZSM-5 catalysts prepared with different methods. *Appl. Catal. B: Environmental*, 26(4): L227-L239.
- Wang, S. and Guin, J. A. (2001). Si-MCM41 Supported Sulfated Zirconia and Nafion for Ether Production. *Energy & Fuels* 15: 666-670.
- Wang, Y. Chen, Q. Yang, W. Xie, Z. Xu, W. and Huang, D. (2003). Effect of support nature on WO_3/SiO_2 structure and butene-1 metathesis. *Appl. Catal. A: General* 250(1): 25-37.
- Wang, W., Wang, J. H., Chen, C. L., Xu, N. P. and Mou, C. Y. (2004). *n*-Pentane isomerization over promoted SZ/MCM-41 catalysts. *Catal. Today* 97(4): 307-313.
- Waqif, M., Bachelier, J., Saur, O., and Lavalley, J. C. (1992). Acidic properties and stability of sulfate-promoted metal oxides. *J. Mol. Catal.* 72: 127-138.
- Weissermel, K. and Arpe, H.-J. (2003). *Industrial Organic Chemistry*, 4th ed. Wiley-VCH: Weinheim, p 167 and 302.

- Wu, P., Tatsumi, T., Komatsu, T. and Yashima, T. (2001). A Novel Titanosilicate with MWW Structure: II. Catalytic Properties in the Selective Oxidation of Alkenes. *J. Catal.* 202: 245–255
- Wu, P. and Tatsumi, T. (2002). Unique *trans*-Selectivity of Ti-MWW in Epoxidation of *cis/trans*-Alkenes with Hydrogen Peroxide. *J. Phys. Chem. B.* 106(4): 748–753.
- Xu, B. Q. and Sachtler, W. M. H. (1997). Reduction of SO_4^{2-} Ions in Sulfated Zirconia Catalysts. *J. Catal.* 167: 224–233.
- Xu, B., Dong, L., Fan, Y. and Chen, Y. (2000). A Study on the Dispersion of NiO and/or WO_3 on Anatase. *J. Catal.* 193(1) 88–95
- Yadav, G. D. and Nair, J. J. (1999). Sulfated zirconia and its modified versions as promising catalysts for industrial processes. *Microporous and Mesoporous Mater.* 33: 1–48.
- Yang, H., Lu, R., Zhao, J., Yang, X., Shen, L. and Wang, Z. (2003). Sulfated binary oxide solid superacids. *Mater. Chem. and Physics* 80: 68–72.
- Yori, J. C., Vera, C. R. and Parera, J. M. (1997). *n*-butane isomerization on tungsten oxide supported on zirconia. *Appl. Catal. A: General* 163(1–2): 165–175.
- Zecchina, A., Bordiga, S., Spoto, G., Marchese, L., Petrini, G., Leofanti, G., Padovan, M. (1992a). Silicalite characterization. 1. Structure, adsorptive capacity, and IR spectroscopy of the framework and hydroxyl modes. *J. Phys. Chem.* 96(12): 4985–4990.
- Zecchina, A., Bordiga, S., Spoto, G., Marchese, L., Petrini, G., Leofanti, G., Padovan, M. (1992b). Silicalite characterization. 2. IR spectroscopy of the interaction of carbon monoxide with internal and external hydroxyl groups. *J. Phys. Chem.* 96(12): 4991–4997.
- Zecchina, A., Bordiga, S., Lamberti, C., Ricchiardi, G., Lamberti, C., Ricchiardi, G., Scarano, D., Petrini, G., Leofanti, G. and Mantegazza, M. (1996). Structural characterization of Ti centres in Ti-silicalite and reaction mechanisms in cyclohexanone ammoximation. *Catal. Today.* 32: 97–106.
- Zhang, F., Guo, X., Wang, X., Li, G., Zhao, Q., Bao, X., Han, X. and Lin, L. (2000). Preparation of titanium-containing zeolites with MEL structure from B-ZSM-11 and their characterization. *Appl. Catal. A: General.* 192: 157–163.

- Zhang, J., Hu, Y., Matsuoka, M., Yamashita, H., Minagawa, M., Hidaka, H. and Anpo, M. (2001). Relationship between the Local Structures of Titanium Oxide Photocatalysts and Their Reactivities in the Decomposition of NO. *J. Phys. Chem. B.* 105(35): 8395-8398.
- Zhanpeisov, N. U. and Anpo, M. (2004). Hydrogen Bonding versus Coordination of Adsorbate Molecules on Ti-Silicalites: A Density Functional Theory Study. *J. Am. Chem. Soc.* 126: 9439-9444.
- Zhuang, J., Yan, Z., Liu, X., Liu, X., Han, X., Bao, X. and Mueller, U. (2002). NMR Study on the Acidity of TS-1 Zeolite. *Catal. Lett.* 83(1): 87-91.
- Zhuang, J., Ma, D., Yan, Z., Liu, X., Han, X., Bao, X., Zhang, Y., Guo, X. and Wang, X. (2004). Effect of acidity in TS-1 zeolites on product distribution of the styrene oxidation reaction. *Appl. Catal. A: General* 258(1): 1-6.
- Ziolek, M., Sobczak, I., Lewandowska, A., Nowak, I., Decyk, P., Renn, M. and Jankowska, B. (2001). Oxidative properties of niobium-containing mesoporous silica catalysts. *Catal. Today* 70(1-3): 169-181.
- Ziolek, M. (2003). Niobium-containing catalysts - the state of the art. *Catal. Today* 78(1-4): 47-64.