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# **SCIENTIFIC BASES FOR THE PREPARATION OF HETEROGENEOUS CATALYSTS**

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## Contents

Foreword	v
Aspects of scale-up of catalyst production <i>Keld Johansen</i>	1
Quantitative structure-activity relationships in zeolite-based catalysts: influence of framework structure <i>J.L. Casci and M.D. Shannon</i>	17
Cogelation: an effective sol-gel method to produce sinter-proof finely dispersed metal catalysts supported on highly porous oxides <i>B. Heinrichs, S. Lambert, C. Alié, J.P. Pirard, G. Beketov, V. Nehasil and N. Kruse</i>	25
Steam reforming of CH <sub>4</sub> over Ni/Mg-Al catalyst prepared by spc-method from hydrotalcite <i>T. Shishido and K. Takehira</i>	35
Toward a molecular understanding of noble metal catalyst impregnation <i>J.R. Regalbuto, M. Schrier, X. Hao, W.A. Spieker, J.G. Kim, J.T. Miller and A.J. Kropf</i>	45
Support modification of cobalt based slurry phase Fischer-Tropsch catalysts <i>S. Barradas, E.A. Caricato, P.J. van Berge and J. van de Loosdrecht</i>	55
The effects of nature and pretreatment of surface alumina support on the catalytic nickelsilicate membrane formation <i>C. Constantin, V. Parvulescu, A. Bujor, G. Popescu and B.L. Su</i>	67
Supports and catalysts preparation by using metal alkoxides grafting technique <i>E. Santacesaria, A. Sorrentino, M. Di Serio and R. Tesser</i>	77
Combinatorial approaches for speeding up heterogeneous catalyst discovery, optimisation and scaling-up <i>C. Mirodatos</i>	89
High surface area metal oxides from matrix assisted preparation in activated carbons <i>M. Schwickardi, T. Johann, W. Schmidt, O. Busch and F. Schüth</i>	93
Effects of the impregnating and drying process factors on mechanical properties of a PCoMo/Al <sub>2</sub> O <sub>3</sub> hydrotreating catalyst <i>Dongfang Wu and Yongdan Li</i>	101

Influence of CeO <sub>2</sub> content on Rh/TiO <sub>2</sub> monolithic catalysts for N <sub>2</sub> O decomposition <i>S. Suarez, M. Yates, F.J. Gil Llambías, J.A. Martín, P. Avila and J. Blanco</i>	111
Pt combustion catalysts prepared from W/O microemulsions <i>J. Rymes, G. Ehret, L. Hilaire and K. Jirátová</i>	121
Preparation of stable catalysts for N <sub>2</sub> O decomposition under industrial conditions <i>S. Alini, F. Basile, A. Bologna, T. Montanari and A. Vaccari</i>	131
The Anderson-type heteropolyanions in the synthesis of alumina- and zeolite-supported HDS oxidic precursors <i>E. Payen, G. Plazenet, C. Martin, C. Lamonier, J. Lynch and V. Harlé</i>	141
Sol-gel preparation of pure and silica-dispersed vanadium and niobium catalysts active in oxidative dehydrogenation of propane <i>P. Moggi, G. Predieri, D. Cauzzi, M. Devillers, P. Ruiz, S. Morselli and O. Ligabue</i>	149
Preparation of nickel-modified ceramic filters by the urea precipitation method for tar removal from biomass gasification gas <i>D.J. Draelants, Y. Zhang, H. Zhao and G.V. Baron</i>	159
Preparation of gold-titanosilicate catalysts for vapor-phase propylene epoxidation using H <sub>2</sub> and O <sub>2</sub> <i>A.K. Sinha, S. Seelan, S. Tsubota and M. Haruta</i>	167
Sol-gel synthesis of colloids and triflates containing hybrid type catalysts <i>A.N. Parvulescu, B.C. Gagea, M. Alifanti, V. Parvulescu and V.I. Parvulescu</i>	177
Preparation of zeogrids through interposed stapling and fusion of MFI zeolite type nanoslabs <i>S.P.B. Kremer, C.E.A. Kirschhock, M. Tielen, F. Collignon, P.J. Grobet, P.A. Jacobs and J.A. Martens</i>	185
Large scale synthesis of carbon nanofibers by catalytic decomposition of hydrocarbon <i>L. Pesant, G. Wine, R. Vieira, P. Leroi, N. Keller, C. Pham-Huu and M.J. Ledoux</i>	193
Synthesis and characterization of carbon nanofiber supported ruthenium catalysts <i>M.L. Toebe, F.F. Prinsloo, J.H. Bitter, A.J. van Dillen and K.P. de Jong</i>	201
Synthesis of high pore volume and specific surface area mesoporous alumina <i>L. Sicard, B. Lebeau, J. Patarin and F. Kolenda</i>	209

Investigation on acidity of zeolites bound with silica and alumina <i>X. Wu, A. Alkhalwaldeh and R.G. Anthony</i>	217
Preparation of BN catalyst supports from molecular precursors. Influence of the precursor on the properties of the BN ceramic <i>J.Á. Perdigon-Melon, A. Auroux, J.M. Guil and B. Bonnetot</i>	227
Monitoring of the particle size of MoS <sub>x</sub> nanoparticles by a new microemulsion-based synthesis <i>K. Marchand, M. Tarret, L. Normand, S. Kasztelan and T. Cseri</i>	239
Transition metal phosphides. Novel hydrodenitrogenation catalysts <i>V. Zuzaniuk, R. Prins, C. Stinner and T. Weber</i>	247
The application of non-hydrothermally prepared stevensites as support for hydrodesulfurization catalysts <i>M. Sychev, R. Prihod'ko, A. Koryabkina, E.J.M. Hensen, J.A.R. van Veen and R.A. van Santen</i>	257
NiMo/HNaY(s)-Al <sub>2</sub> O <sub>3</sub> catalysts for the hydrodesulfurization of hindered dibenzothiophenes: effect of the preparation method <i>T. Klimova, D. Solis, J. Ramírez and A. López-Agudo</i>	267
Chiral dirhodium catalysts confined in porous hosts <i>H.M. Hultman, M. de Lang, M. Nowotny, I.W.C.E. Arends, U. Hanefeld, R.A. Sheldon and T. Maschmeyer</i>	277
Synthesis and characterization of zeolite encaged enzyme-mimetic copper histidine complexes <i>J.G. Mesu, H.J. Tromp, D. Baute, E.E. van Faassen and B.M. Weckhuysen</i>	287
Strategies for the heterogenization of rhodium complexes on activated carbon <i>J.A. Diaz-Auñon, L.C. Román-Martínez, C. Salinas-Martínez de Lecea and H. Alper</i>	295
Heterogeneous metathesis initiators <i>M. Mayr, B. Mayr and M.R. Buchmeiser</i>	305
Preparation of physically heterogeneous and chemically homogeneous catalysts on the base of metal complexes immobilized in polymer gels <i>A.A. Efendiev, T.N. Shakhtakhtinsky and N.A. Zeinalov</i>	313
Hydrocracking catalyst to produce high quality diesel fraction <i>R. Galiasso Tailleux</i>	321

Thermostable yttria-doped inorganic oxide catalyst supports for high temperature reactions <i>E. Elaloui, R. Begag, B. Pommier and G.M. Pajonk</i>	331
Preparation and characterization of $\text{WO}_x$ - $\text{CeO}_2$ catalysts <i>M. Alifanti, C.M. Visinescu, V.I. Parvulescu, P. Grange and G. Poncelet</i>	337
Preparation of iridium catalysts by deposition precipitation: room temperature oxidation of CO <i>M. Okumura, E. Konishi, S. Ichikawa and T. Akita</i>	345
New approach to preparation and investigation of active sites in sulfated zirconia catalysts for skeletal isomerization of alkanes <i>N.A. Pakhomov, A.S. Ivanova, A.F. Bedilo, E.M. Moroz and A.M. Volodin</i>	353
Supported ruthenium carbido-cluster catalysts for the catalytic removal of nitrogen monoxide and sulfur dioxide: the preparation process monitored by sulfur K-edge X-ray absorption near-edge structure <i>Y. Izumi, T. Minato, K.-I. Aika, A. Ishiguro, T. Nakajima and Y. Wakatsuki</i>	361
Catalytic transformation of dichloromethane over Y and X zeolites <i>L. Pinard, J. Mijoin, R. Lapeyrolerie, P. Magnoux and M. Guisnet</i>	369
Preparation of new solid super-acid catalyst, titanium sulfate supported on zirconia and its acid catalytic properties <i>J.R. Sohn, E.H. Park and J.G. Kim</i>	377
Superacid $\text{WO}_x/\text{ZrO}_2$ catalysts for isomerization of n-hexane and for nitration of benzene <i>V.V. Brei, O.V. Melezhyk, S.V. Prudius, M.M. Levchuk and K.I. Patryliak</i>	387
Preparation of copper-oxide catalyst systems for hydrogenation <i>Y. Sakata, N. Kouda, Y. Sakata and H. Imamura</i>	397
Application of experimental design for $\text{NO}_x$ reduction by Pd-Cu catalysts <i>M. Rebollar, M. Yates and M.A. Valenzuela</i>	407
Marked difference of catalytic behavior by preparation methods in $\text{CH}_4$ reforming with $\text{CO}_2$ over $\text{Mo}_2\text{C}$ and WC catalysts <i>S. Naito, M. Tsuji, Y. Sakamoto and T. Miyao</i>	415
Synthesis and properties of new catalytic systems based on zirconium dioxide and pentasils for process of $\text{NO}_x$ selective catalytic reduction by hydrocarbons <i>V.L. Struzhko, S.N. Orlyk, T.V. Myroniuk and V.G. Ilyin</i>	425

Preparation of chitosan based catalysts for several reactions of liquid phase hydrogenation <i>V. Isaeva, A. Ivanov, L. Kozlova and V. Sharf</i>	435
Preparation of Mo/Al <sub>2</sub> O <sub>3</sub> sulfide catalysts modified by Ir nanoparticles <i>J. Cinibulk and Z. Vit</i>	443
Peptization mechanisms of boehmite used as precursors for catalysts <i>D. Fauchadour, F. Kolenda, L. Rouleau, L. Barré and L. Normand</i>	453
Influence of the treatment of Y zeolite by ammonium hexafluorosilicate on physicochemical and catalytic properties: application for chlororganics destruction <i>R. Lopez-Fonseca, J.I. Gutiérrez-Ortiz, B. de Rivas, S. Cibrian and J.R. González-Velasco</i>	463
Preparation of SiO <sub>2</sub> modified SnO <sub>2</sub> and ZrO <sub>2</sub> with novel thermal stability <i>Y.-Z. Zhu, J.-Y. Wei, L. Zeng, X.-D. Zhao, W. Lin and Y.-C. Xie</i>	471
Control of the textural properties of cesium 12-molybdophosphate-based supports <i>S. Paul, V. Dubromez, L. Zair, M. Fournier and D. Vanhove</i>	481
MnO <sub>x</sub> /CeO <sub>2</sub> -ZrO <sub>2</sub> and MnO <sub>x</sub> /WO <sub>3</sub> -TiO <sub>2</sub> catalysts for the total oxidation of methane and chlorinated hydrocarbons <i>E. Kantzer, D. Döbber, D. Kiessling and G. Wendt</i>	489
Catalytic behaviour of Rh-supported catalysts on lamellar and zeolitic structures by anchoring of organometallic compound <i>C. Blanco, R. Ruiz, C. Pesquera and F. Gonzalez</i>	499
The use of sol-gel technique to prepare the TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> binary system over a wide range of Ti-Al ratios <i>A.Yu. Stakheev, G.N. Baeva, N.S. Telegina, I.V. Mishin, T.R. Brueva, G.I. Kapustin and L.M. Kustov</i>	509
Catalytic performance in the complete acetone oxidation of manganese and cobalt oxides supported on alumina and silica <i>A. Gil, S.A. Korili, M.A. Vicente and L.M. Gandia</i>	517
Unsupported and supported manganese oxides used in the catalytic combustion of methyl-ethyl-ketone <i>L.M. Gandia, S.A. Korili and A. Gil</i>	527
Ni/H $\beta$ zeolite catalysts prepared by the deposition-precipitation method <i>R. Nares, J. Ramirez, A. Gutierrez-Alejandre, R. Cuevas, C. Louis and T. Klimova</i>	537

Sol-gel $\text{Al}_2\text{O}_3$ structure modification by Ti and Zr addition. A NMR study <i>J. Escobar, J.A. de Los Reyes and T. Viveros</i>	547
Promotion of Ru/ $\text{ZrO}_2$ catalysts by platinum <i>A.M. Serrano-Sánchez, F. Blas-Suárez, P. Steltenpohl, M.P. González-Marcos, J.A. González-Marcos, and J.R. González-Velasco</i>	555
Catalysts based on $\text{RhMo}_6$ heteropolymetalates. Bulk and supported preparation and characterisation <i>C.I. Cabello, I.L. Botto, M. Muñoz and H.J. Thomas</i>	565
Metallosilicate mesoporous catalysts prepared by incorporation of transition metals in the MCM-41 molecular sieves and their catalytic activity in selective oxidation of aromatics (styrene and benzene) <i>V. Parvulescu and B.L. Su</i>	575
Controlled surface modification of alumina-supported Mo or Co-Mo sulfides by surface organometallic chemistry <i>J.-S. Choi, C. Petit-Clair and D. Uzio</i>	585
Novel one step synthesis of cobalt (II) phthalocyanine-hydrotalcite catalysts for mercaptan oxidation in light oil sweetening <i>I. Chatti, A. Ghorbel and J.M. Colin</i>	595
Structural and catalytic properties of Zr-Ce-Pr-O xerogels <i>S. Rossignol, C. Descorme, C. Kappenstein and D. Duprez</i>	601
Influence of the precursor (nature and amount) on the morphology of $\text{MoO}_3$ crystallites supported on silica <i>D. Navez, C. Weinberg, G. Mestl, P. Ruiz and E.M. Gaigneaux</i>	609
Single step synthesis of metal catalysts supported on porous carbon with controlled texture <i>N. Job, F. Ferauche, R. Pirard and J.P. Pirard</i>	619
Ag- $\text{SiO}_2$ and Cu/ $\text{SiO}_2$ cogelled xerogel catalysts for benzene combustion and 2-butanol dehydrogenation <i>S. Lambert, N. Tcherkassova, C. Cellier, F. Ferauche, B. Heinrichs, P. Grange and J.P. Pirard</i>	627
Preparation of zeolite catalysts for dehydrogenation and isomerization of n-butane <i>M. Inaba, K. Murata, M. Saito, I. Takahara, N. Mimura, H. Hamada and Y. Kurata</i>	637

The application of well-dispersed nickel nanoparticles inside the mesopores of MCM-41 by use of a nickel citrate chelate as precursor <i>D.J. Lensveld, J.G. Mesu, A.J. van Dillen and K.P. de Jong</i>	647
Preparation of Ce–Zr–O composites by a polymerized complex method <i>T.G. Kuznetsova, V.A. Sadykov, E.M. Moroz, S.N. Trukhan, E.A. Paukshtis, V.N. Kolomiichuk, E.B. Burgina, V.I. Zaikovskii, M.A. Fedotov, V.V. Lunin and E. Kemnitz</i>	659
Sol–gel routes for the preparation of heterogeneous catalyst based on Ru, Rh, Pd supported metals <i>P. Moggi, S. Morselli and G. Predieri</i>	669
Development of novel heterogeneous catalysts for oxidative reactions: preparation and performance of Co–N <sub>x</sub> catalysts in partial oxidation of toluene and n-butane <i>M.L. Kaliya, S.B. Kogan and M. Herskowitz</i>	679
Synthesis and modification of basic mesoporous materials for the selective etherification of glycerol <i>J.-M. Clacens, Y. Pouilloux and J. Barrault</i>	687
Carbon nanotubes: a highly selective support for the C=C bond hydrogenation reaction <i>J.-P. Tessonnier, L. Pesant, C. Pham-Huu, G. Ehret and M.J. Ledoux</i>	697
Raman studies of the templated synthesis of zeolites <i>P.P.H.J.M. Knops-Gerrits and M. Cuypers</i>	705
Templateless synthesis of catalysts with narrow mesoporous distribution <i>N. Yao, G. Xiong, S. Sheng, M. He and K.L. Yeung</i>	715
Control of pore structures of titanias and titania/aluminas using complexing agents <i>M. Toba, S. Niwa, N. Kijima and Y. Yoshimura</i>	723
Tungstophosphoric acid immobilized in polyvinyl alcohol hydrogel beads as heterogeneous catalyst <i>L.R. Pizzio, C. Cáceres and M.N. Blanco</i>	731
Functionalized SiMCM-41 as support for heteropolyacid based catalysts <i>L.R. Pizzio, A. Kikot, E. Basaldella, P. Vazquez, C. Cáceres and M.N. Blanco</i>	739
Influence of the preparation method on the surface properties and activity of alumina-supported gallium oxide catalysts <i>A. Petre, B. Bonnetot, A. Gervasini and A. Auroux</i>	747



Preparation and properties of bimetallic Ru–Sn sol–gel catalysts: the influence of catalyst reduction <i>J. Hajek, N. Kumar, H. Karhu, L. Cervený, J. Vayrynen, T. Salmi and D. Yu. Murzin</i>	757
A new insight into molybdate/boehmite interaction <i>D. Minoux, F. Diehl, P. Euzen, J.-P. Jolivet and E. Payen</i>	767
Controlled coating of high surface area silica with titania overlayers by atomic layer deposition <i>J. Keränen, E. Iiskola, C. Guimon, A. Auroux and L. Niinistö</i>	777
Concept of the synthesis of novel platinum catalysts for selective hydrogenation of unsaturated carbonyl compounds <i>J. Kijenski and P. Winiarek</i>	787
Storage and supply of hydrogen mediated by iron oxide: modification of iron oxides <i>S. Takenaka, C. Yamada, T. Kaburagi and K. Otsuka</i>	795
Catalytic activity of bulk and supported sulfated zirconia <i>I.J. Dijs, L.W. Jenneskens and J.W. Geus</i>	803
New one-step synthesis of superacid sulfated zirconia <i>L. Zanibelli, A. Carati, C. Flego and R. Millini</i>	813
Elaboration and characterization of a realistic Phillips model catalyst for ethylene polymerisation <i>P.G. Di Croce, F. Aubriet, P. Bertrand, P. Rouxhet and P. Grange</i>	823
Preparation of new basic mesoporous silica catalysts by ammonia grafting <i>H. Yoshida, Y. Inaki, Y. Kajita, K. Ito and T. Hattori</i>	837
Titania–silica catalysts prepared by sol–gel method for photoepoxidation of propene with molecular oxygen <i>C. Murata, H. Yoshida and T. Hattori</i>	845
Preparation of large surface area $\text{MnO}_x$ – $\text{ZrO}_2$ for sorptive $\text{NO}_x$ removal <i>M. Machida, M. Uto and T. Kijima</i>	855
Preparation of $\text{CuO}_x$ – $\text{TiO}_2$ nano-composite photocatalysts from intercalated layer structure <i>M. Machida, S. Nagasaki and T. Kijima</i>	863
Vanadia-doped titanium pillared clay: preparation, characterization and SCR activity of NO by ammonia <i>L. Khalfallah Boudali, A. Ghorbel, P. Grange and S.M. Jung</i>	873

- Advanced preparation by sol–gel method of the encapsulated Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for methane combustion  
*S. Fessi, A. Ghorbel, A. Rives and R. Hubaut* 881
- Non-ionic surfactant templated synthesis of mesoporous silica in the presence of platinum salts  
*M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, F.J. Romero and F.J. Urbano* 891
- Synthesis and acid–base properties of catalysts based on magnesium and sodium-magnesium mixed phosphates  
*M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, R. Roldán, F.J. Romero and F.J. Urbano* 899
- Preparation of Pd–Ce/ZrO<sub>2</sub> catalysts for methane oxidation  
*L.S. Escandón, S. Ordóñez, F.V. Díez and H. Sastre* 907
- The effect of cerium introduction on vanadium-USY catalysts  
*C. Ramos Moreira, M. Schmal and M.M. Pereira* 915
- Rh–Co mordenite catalysts for the selective reduction of NO by methane  
*C.E. Quincoces, M. Incolla, A. De Ambrosio and M.G. González* 925
- Surface characterization of WO<sub>3</sub>–TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts and reactivity on selective catalytic reaction of NO by NH<sub>3</sub>  
*S. Egues, N.S. de Resende and M. Schmal* 933
- Catalytic materials for the synthesis of hydrofluorocarbons  
*P. Cuzzato, V. Giammetta, R. Trabace and F. Trifiro* 941
- Preparation, characterization and reactivity in m-cresol methylation of new heterogeneous materials having basic properties  
*F. Cavani, C. Felloni, D. Scagliarini, A. Tubertini, C. Flego and C. Perego* 953
- The effect of glycols in the organic preparation of V/P mixed oxide catalyst for the oxidation of n-butane to maleic anhydride  
*S. Albonetti, F. Cavani, S. Ligi, F. Pierelli, F. Trifiro, F. Ghelfi and G. Mazzoni* 963
- Synthesis and characterization of nanostructured Mo<sub>2</sub>C on carbon material by carbothermal hydrogen reduction  
*C. Liang, Z. Wei, Q. Xin and C. Li* 975
- Carbon composite-based catalysts: new perspectives for the low-temperature H<sub>2</sub>S removal  
*J.-M. Nhut, R. Vieira, N. Keller, C. Pham-Huu, W. Boll and M.J. Ledoux* 983

Active carbon surface oxidation to optimize the support functionality and metallic dispersion of a Pd/C catalyst <i>V. Dubois, Y. Dal and G. Jannes</i>	993
n-Butane isomerization over Al-promoted sulfated zirconias. Influence of the sulfate content <i>J.A. Moreno and G. Poncelet</i>	1003
Influence of preparation procedure on physical and catalytic properties of carbon-supported Pd–Au catalysts <i>P. Canton, F. Menegazzo, M. Signoretto, F. Pinna, P. Riello, A. Bedetti and N. Pernicone</i>	1011
Preparation of mesoporous highly dispersed Pd–Pt catalysts for deep hydrodesulfurization <i>X. Xu, P. Waller, E. Crezee, Z. Shan, F. Kapteijn and J.A. Moulijn</i>	1019
Preparation of highly ordered CMI-1 and wormhole-like DWM mesoporous silica catalyst supports using C <sub>16</sub> (EO) <sub>10</sub> as surfactant <i>A. Léonard, J.L. Blin and B.L. Su</i>	1027
Synthesis and characteriation of nanostructured mesoporous zirconia catalyst supports using non-ionic surfactants as templating agents <i>J.L. Blin, L. Gigot, A. Léonard and B.L. Su</i>	1035
Effect of preparation parameters on the catalytic activities of sulfated ZrO <sub>2</sub> –SiO <sub>2</sub> catalysts obtained by sol–gel process <i>R. Akkari and A. Ghorbel</i>	1045
Non-aggressive way for preparation of zirconium sulfate pillared clay using zirconium acetate developing high sulfur thermal stability over 830°C <i>S. Ben Chaabene, L. Bergaoui, A. Ghorbel and J.F. Lambert</i>	1053
Influence of the preparation conditions on the structure of the active phase and catalytic properties of Ni–Co-molybdate propane oxydehydrogenation catalysts <i>M.M. Barsan, A. Maione and F.C. Thyron</i>	1063
Oxidized diamond as a new catalyst support <i>T. Suzuki, K. Nakagawa, N.-O. Ikenaga and T. Ando</i>	1073
Preparation of catalytic membranes, micro-capsules and fabrics active in immobilized Fenton chemistry <i>J. Fernandez, V. Nadtochenko, A. Bozzi, T. Yuranova and J. Kiwi</i>	1081
Preparation of vanadium-based catalysts for selective catalytic reduction of nitrogen oxides using titania supports chemically modified with organosilanes <i>H. Kominami, M. Itonaga, A. Shinonaga, K. Kagawa, S. Konishi and Y. Kera</i>	1089

Design, preparation and testing of effective  $\text{FeO}_x/\text{SiO}_2$  catalysts in methane to formaldehyde selective oxidation

*F. Arena, F. Frusteri, L. Spadaro, A. Venuto and A. Parmaliana* 1097

New Fe–Mo–Ti mixed oxides prepared via the sol–gel method: comparison of the textural properties with solids obtained by impregnation

*S.R.G. Carrazan, C. Martin, C. M. Pedrero and J. Saunders* 1107

Index 1115

## **Aspects of scale-up of catalyst production**

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### **1. SCOPE OF CATALYST PRODUCTION**

Catalyst production has a significant influence on the economy, since 80-90% of the chemicals used in a modern society are exposed to a catalyst. The value of the US catalyst market was 2.2 billion \$ in 2000 [1]. A number of specialised catalyst companies in the world, many global, produce and supply a large number of products to the industry. It is said that products corresponding to 10% of the GNP of the industrialised countries are dependent on the availability of catalyst. Catalyst plants produce quantities of 0.1-100 t/day of each product dependant on the type. Thus, transfer of new products and implementation in catalyst plants are important technological disciplines for each catalyst company.

### **2. NATURE OF THE SCALE-UP PROBLEM**

Before the decision is taken on transferring a new recipe from research and development departments to an existing catalyst plant or a new investment, considerable work has already been carried out – many test samples have been prepared and activity-tested. All candidates for a new product have one thing in common: in the starting phase they have been prepared and selected from the laboratory processes.

#### **2.1. Description of laboratory prepared samples**

Laboratory or bench scale prepared catalyst samples for screening are typically made in gram scale (10-50 g). The catalysts can be prepared in many ways depending on the type, but steps for three commonly used preparation routes are shown below in Fig. 1 and, for each step, examples of the typical laboratory equipment are given.

### I. Typical co-precipitated catalyst manufacture

Preparation step	Typical equipment
1. Dissolution of agents	Beaker with stirrer
2. Precipitation	Pump + beaker with stirrer
3. Ageing	Electric heating, thermostatic bath
4. Filtration	Buchner funnel
5. Washing	Demineralised water on Buchner funnel
6. Drying	Drying cabinet
7. Calcination	Muffle furnace
8. Lubricant aid addition	Powder mixer
9. Tableting	Single station excenter press
10. Calcination	Electrically heated muffle furnace
11. Activation	Small reactor with H <sub>2</sub> /N <sub>2</sub> once through

### II. Typical impregnated catalyst carrier process

Preparation step	Typical equipment
1. Forming a support (from another route)	
2. Activation of support	Heated muffle furnace
3. Dissolution of impregnation liquid(s)	Beaker with stirrer (pure chemicals)
4. Impregnation	Net in a beaker
5. Drying	Drying cabinet
6. Decomposition	Muffle furnace
7. Re-impregnation back to 4.	
8. Activation	Reactor sulphidation with H <sub>2</sub> /N <sub>2</sub> once through

### III. Typical process for mixed/compounded catalyst

Preparation step	Typical equipment
1. Powders	From flasks
2. Dissolution of active metals	Beaker with stirrer
3. Dissolution of extrusion aids	Beaker with stirrer
4. Mixing	Laboratory kneader
5. Extrusion	Laboratory piston extruder
6. Drying	Drying cabinet
7. Calcination/decomposing	Muffle furnace
8. Sieving	Laboratory sieve
9. Activation	Small reactor with H <sub>2</sub> /N <sub>2</sub> etc. once through

Fig. 1. Three examples of commonly used preparation methods

The laboratory equipment used is normally characterised by:

- Small dimensions with short mass and heat transport distances
- High energy intensity per volume for stirrer mixers and kneaders
- Pure chemicals
- Small layers in muffle furnaces with low temperature gradients, but long heating cycle
- $H_2$  activation with low  $p_{H_2O}$
- Drying with low but undefined  $p_{H_2O}$
- Precipitation within small volume dimension
- Filtration without respect of agglomerate size
- Washing without respect of time or leakage of particles or ions
- Tableting/forming of non-representative granules
- Generated heat during processes easily dissipated to cooling surface

A modern catalyst laboratory will analyse and describe in detail all intermediates and final catalysts from the above three manufacturing routes by means of the methods as follows: main chemical elements and trace elements, phases (if not amorphous), pore distribution and BET or selective surface area. A more complete list of commonly used methods is given in Table 1 below:

Table 1.

Physical and chemical characterisation methods

<b>Chemical</b>	
Main chemical elements	ICP, AAS, XRF and electron micro probe analysis
Trace elements	AAS, ICP
Oxidation state	Electron micro probe analysis, EDS in SEM, EDS in TEM
Element distribution	
<b>Physical</b>	
Surface area	BET ( $N_2$ , Ar, K), or specific area, chemisorption of $H_2$ , CO, $N_2O$
Pore volume - total	Water absorption -Hg intrusion
Pore size distribution	He, or Hg intrusion, $N_2$ adsorption
Phases, crystallite size	XRD, TEM, Raman Spectroscopy
Surface composition	XPS, SIMS
Surface properties	IR, microcalorimetry, chemisorption/desorption (TPD, TPR)
Particle size distribution	LLD, SAXS, sieves, TEM, SEM
Structure and texture	TEM, SEM, optical microscopy
Thermogravimetry	TGA, DTA, dilatometer
Specially for finished product form	
Abrasion resistance for granules	
Attrition resistance for fluid cat and powders	Attrition loss
Crushing strength	Texture analyser

However, all the above methods in Table 1 cannot give a scientifically exhaustive description of the intermediates nor of the final catalyst. Amorphous phases often obtained from precipitation cannot be characterised sufficiently (how many kinds of amorphous phases exist?) Furthermore, the final catalyst granule is formed from agglomerates of crystallites. Both crystallites (forming primary agglomerates) and the agglomerates have their own particle size distribution and binding properties. Particle size distribution of primary and secondary agglomerates controls the final pore size distribution. The pore size distribution and particle strength will have significant influence on the final performance of the product in the reactor. Even considering the methods listed in Table 1, there is no method or combined methods today that can give a full description of the crystallite-agglomerate multi-parameter system. To further illustrate the problem, it should be mentioned that even if the overall chemical composition is the same for two different manufacturing routes, the pore size distribution is most probably different. *Thus, it is not possible to characterise an intermediate or final catalyst so you can be sure to have the same catalyst without preparing it in the same reproducible way.*

## 2.2 Catalyst manufacturing – unit operations

The catalyst plant is operating in ton scale (typically 1-100 t/day) with processes and equipment completely different from bench scale as sketched in Fig. 1, even if the preparation steps are the same. In the open literature, description of catalyst manufacturing processes and equipment is sparse. The reference list contains important monographs and papers [2-24]. The patent literature gives some information, but catalyst manufacturing technologies are often not patented but kept secret. The single step in manufacturing is called a unit operation and can be performed by several types of equipment. Table 2 shows most of the unit operations used and examples of equipment for each. Most of the typical equipment will have more different time constants, heat transfer, flow patterns, temperature profiles etc. than bench scale equipment and, therefore, the final catalyst will achieve other properties.

## 2.3 Optimal combinations

For every commercial catalyst an optimal combination of unit operation sequence exists for the manufacture of that specific catalyst and there will for each unit operation exist preferential process equipment, i.e. fluid bed calciner for calcination. The sequence of unit operations with the special selection of process equipment and all process parameters forms the *know-how* for manufacturing a catalyst product of large commercial value. But know-how does not mean that you always know why the desired properties are obtained due to the insufficient scientific characterisation of the catalyst material as described above under 2.1. Even small adjustments of the process can change strength, pore size distribution, bulk density, crystallite size etc. of the product and, thus, harm the performance in the industrial reactor. It has normally been costly and time-consuming to reach the final recipe and, therefore, all catalyst companies want to keep it secret. *If a single unit operation is changed it will often influence the optimisation of most of the other unit operations, and much of the development will have to be redone.*



Table 2.  
List of unit operations with typical equipment

Unit operation	Typical equipment
1. Dissolution	Tanks with stirrer
2. Precipitation	Pumps, specially designed reactors and stirrers
3. Ageing and maturation, gel formation	Temperature-regulated tanks, autoclaves
4. Filtration	Belt filter Drum filter Centrifuge Filter press
5. Washing	Belt filter Drum filter Centrifuge
6. Drying	Belt conveyor furnace Spray drying Fluid bed drying Rotary kiln Vacuum dryer
7. Wet mixing (kneading)	Z-mixer Double screw mixer
8. Dry mixing	Nauta mixer Double cone mixer Ribbon blender
9. Grinding	Jet mill Roller mill Universal mill Pearl mill
10. Sieving	Screen
11. Forming	Tabletting Extrusion Granulation Spray drying Corrugation
12. Calcination	Belt conveyor furnace Rotary kiln Shaft furnaces Chamber and muffle furnace Tunnel furnace Fluid bed
13. Impregnation	Pore filling – incipient wetness Immersion in liquid Controlled chemisorption
14. Decomposition	See under calcination
15. Fusion	Electrical hearth
16. Activation	Prereduction reactor
17. Cooling and annealing	Fluid bed, chamber and muffle furnace
18. Coating	Washcoater, dragee pan
19. Leaching	Tanks with stirrer
20. Reslurrying	Tanks with stirrer, kneader