Catalysis Today 137 (2008) 132–143

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Aqueous synthesis of high surface area metal oxides

Christian Bluthardt [b], Carola Fink [a], Klemens Flick [b], Alfred Hagemeyer [a,*], Marco Schlichter [a], Anthony Volpe Jr. [a]

[a] *Symyx Technologies Inc., 3100 Central Expressway, Santa Clara, CA 95051, USA*
[b] *University of Applied Science, Max-Planck-Street 39, D-74081 Heilbronn, Germany*

ARTICLE INFO

Keywords:
High surface area
Metal oxides
High throughput
Combinatorial
Pechini
Combusion synthesis
Catalysts
Absobents
Carriers
Supports

ABSTRACT

By applying high throughput synthesis and characterization technologies, we have been optimizing common dry or aqueous synthetic routes for the preparation of high surface area metals and oxides, such as precipitation and modified Pechini methods. For wet combustion synthesis, we have been screening a variety of organic acids as dispersants and developed proprietary recipes for individual metals. By resorting to easily decomposable organic acids (as opposed to citric acid in the original Pechini combustion method), such as glyoxylic acid, oxalacetic acid and ketoglutaric acid, it is possible to obtain high surface area materials for many metals after careful optimization of acid/metal ratio and calcination conditions. Examples are Sn, In, Co, Ru, Ni, Fe, Mn, Y, Ce and Rare Earth oxides and their mixtures. After calcination in the temperature range of about 300–400 °C, surface areas >150 m^2/g could be obtained for Er, Tm, Co, Ru, and Nb; >200 m^2/g for Sn, Fe, Mn, and Y; >300 m^2/g for Ce; and >400 m^2/g for Ni oxide. Noteworthy are also >140 m^2/g for La_2O_3, >80 m^2/g for CuO, and 75 m^2/g for ZnO. For V, around 40 m^2/g was possible for the nearly carbon-free V_2O_5, whereas up to 90 m^2/g was obtained for a 90% V–10% carbon composite (by incomplete combustion of the organic acid). Residual carbon helps in stabilizing the porous oxide against sintering. Thus, conventional aqueous routes (precipitation, Pechini) can be competitive to more elaborate and costly methods such as those using organic solvents, sol–gel, supercritical drying or template/hydrothermal synthesis. Combustion synthesis is well suited for the preparation of mixed oxides from mixed metal solutions in aqueous organic acids. Bulk porous Co and CoRu mixed oxides have been screened for liquid phase alcohol oxidations and CoRuCe oxides for CO oxidation and VOC destruction, and doped NiO has been reduced to the metal and tested for various hydrogenations.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

High surface area metal oxides are desirable absorbents, carriers and catalysts, and various synthetic methods starting from aqueous metal solutions or slurries have been applied. These include precipitation, hydrothermal synthesis, microemulsions as well as wet combustion synthesis. Auxiliary reagents such as acids or bases, templates, surfactants or dispersing agents are added to convert, immobilize or finely divide the metal precursors that upon subsequent drying and calcination are transformed to the corresponding oxides.

Organic solvent assisted routes such as solvothermal synthesis, sol–gel with or without supercritical drying, or oil drop methods are also widely used for the preparation of high surface area materials. The various traditional synthetic methods that are available for the synthesis of inorganic nanoparticles have been extensively reviewed and evaluated [1,2]. Recently many more sophisticated methods for the preparation of nanoparticulated materials have been proposed, e.g. flame pyrolysis, arc and plasma discharge, sputtering, microwave irradiation, molten salt flux methods, solid state reactions, mechanical alloying, and inert gas condensation.

We have investigated the potential of three different traditional (dry or aqueous) routes, namely dry decomposition, precipitation and combustion synthesis from aqueous solutions, for the synthesis of high surface area metals and oxides starting from common and readily available metal precursors without making use of expensive templates, surfactants or alcoholic solvents or supercritical drying or high pressure equipment.

For liquid-phase combustion synthesis, we have been screening a variety of organic acids as dispersants and developed proprietary recipes for individual metals. Combustion synthesis is well suited for the preparation of mixed oxides from mixed metal solutions in aqueous organic acids. By resorting to easily decomposable organic acids (as opposed to citric acid in the original Pechini combustion

---

* Corresponding author.
E-mail address: avolpe@symyx.com (A. Hagemeyer).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.04.045

method [1–5] or malic acid in a later modification [6]), such as glyoxylic acid and ketoglutaric acid, it was possible to obtain high surface area materials for many metals after careful optimization of acid/metal ratio and calcination conditions [7–18], for example, Sn, In oxides and their mixtures [8,9,12,14], yttria [15] and ceria [18]. Some catalytic applications of these high surface area metal oxides have already been published, for example, SnO_2 as carrier for emissions control [12], ceria as carrier for water–gas-shift catalysts [19], and Co–Ru mixed oxides for CO and total oxidations [20,21]. We have now applied and optimized combustion synthesis methods for additional metals such as Ni, Co, Fe, and Rare Earths and compared surface areas to those obtained by precipitation. We will summarize previous and recent results, classify metals according to most suitable acid dispersant and corresponding calcinations conditions and point out common trends.

2. Experimental

2.1. Equipment

2.1.1. Precipitation

Our integrated co-precipitation workflow has been published elsewhere [17,18]. Briefly, the workflow consists of an automated co-precipitation station, an automated particle recovery station, ovens for thermal treatment, and a parallel sample agglomeration and sizing system for particle sizing. The Symyx Software suite is used to design the, control the robotic actions and store the resulting data, and view the data. The co-precipitation station consists of a robot with eight parallel precipitation channels and 8 columns of 8 precipitation wells resulting in an 8 × 6 array of wells. Each channel has a pH probe, temperature probe, and three liquid addition probes that are robotically inserted into a disposable liner with magnetically coupled stirring. The Station is shown in Fig. 1. The precipitation can be carried out as a constant liquid addition, as a titration, or as a constant pH precipitation.

Precipitation or pH titration recipes were then scaled up in 250 ml three-neck flasks equipped with masterflex pH controllers and peristaltic pumps. Isolation of the precipitate was done by centrifugation in two 40 ml vials followed by 4 wash steps in 40 ml vials. A typical temperature ramp was as follows: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/350 °C/4 h hold in 40 ml vial.

2.1.2. Combustion synthesis

Libraries consisting of arrays of stirred tall 40 ml glass vials were loaded by powder or liquid dispensing robots with solid metal precursors and/or metal solutions as well as aqueous solutions of organic dispersants and/or solid organics, optionally aged at room temperature in open vials to evaporate part of the solvent (to induce gelation but also to prevent splashing and excessive foaming during the subsequent drying step), then dried and calcined in air in static calcination ovens. Amounts and process conditions used are detailed in the following tables.

2.2. Synthesis recipes

2.2.1. Dry decomposition

Common metal salts such as oxalate, acetate, carbonate, hydroxide were purchased from Aldrich, Alfa or Pfaltz&Bauer and used as supplied. Metal formates were prepared by slurrying metal carbonate or hydroxide in excess formic acid followed by solvent evaporation. The dry powders were calcined in air in tall 40 ml vials according to the following representative heat up protocol: 55 °C/1 h ramp/120 °C/1 h hold/1 h ramp/325 °C/4 h hold.

2.2.2. Wet combustion synthesis

A general recipe consists of dissolving or slurrying the metal precursor (acetate, nitrate, hydroxide) in aqueous organic acid (glyoxylic acid OHC-COOH, ketoglutaric acid or acetone-1,3-dicarboxylic acid $HOOC\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}COOH$, oxalacetic acid $HOOC\text{-}CH_2\text{-}CO\text{-}COOH$) in a tall 40 ml glass vial followed by calcination in air. A typical heat up protocol is as follows: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/300 °C/4 h hold.

2.2.3. Synthesis of Ni–Ce–Pd by the modified Pechini method

1 g Ni hydroxide was dissolved in 6.5 ml 20% aq. glyoxylic acid in a 40 ml glass vial, then appropriate amounts of solid Ce acetate and ammonium Pd oxalate were added under stirring to obtain a

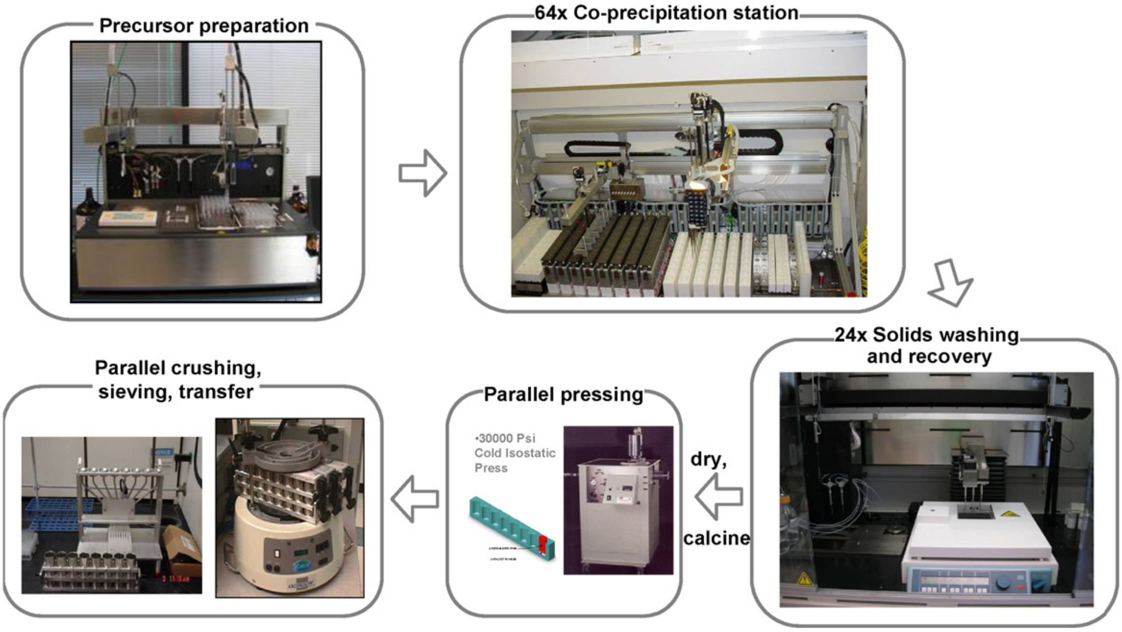


Fig. 1. Co-precipitation station and supporting catalyst synthesis hardware.

clear green solution that was calcined at 320 °C for 4 h in air in a static calcinations oven using the standard heat up ramp mentioned above in 2.2. Ce contents varied from 1 to 6 wt% while Pd contents were in the range 0.02–0.2 wt%.

2.3. Characterization

BET surface area, N_2 adsorption isotherms and pores size distributions were measured in a three-channel Micromeritics Tristar 3000 porosity analyzer. Chemical composition and carbon content was analyzed by Galbraith Labs. XRD was recorded on a PANalytical X'Pert Pro and SEM on a Hitachi S4300.

2.4. Integrated workflow and sample throughput

We have focussed on three realistic and therefore commercially relevant synthetic methods and have chosen the screening tools accordingly (co-precipitation robots for the precipitated samples, liquid dispense robots for the metal-acid solutions, and powder dispense robots for the solids). It should be stressed that even the oxides prepared by dry decomposition required a high throughput approach, namely solids handling by powder dispense robots. Hundreds of samples need to be handled and tracked which would be impossible without an integrated workflow. The libraries are, of course, simple arrays of vials. No optimization algorithm or evolutional approach was taken and the multidimensional parameter space mapped out by a straight forward grid search with orthogonal libraries (two gradients per library).

The calcination is very efficient as many arrays of vials can be processed in parallel at the same time in large static ovens. The bottleneck of the workflow was the three-channel BET instrument, where approximately 20 samples could be characterized per day. The libraries (arrays of vials) were manually transferred to the calcination ovens. This step was not automated but was still not the bottleneck since many arrays could be processed in parallel (e.g. a stack of 5 plates of 48 samples each). The workflow was accelerated in many cases by eliminating bad samples based on their color (e.g. holmium should turn pink) and weight (mass balance indicative of complete combustion of organic dispersant). In summary, the time needed to characterize a 24-sample library is roughly 1 day.

The level of reproducibility is approximately 10%. BET strongly depends on the calcination temperature (which therefore must be optimized in small increments of 5–10 K steps), and reproducibility can be poor when using calcination ovens with slightly different actual temperatures from the set value and/or with temperature distributions.

2.5. Catalytic tests

NiO samples were pre-reduced at 250 °C by a continuous flow of 10% H_2 in N_2 and then tested for catalytic activity in the

Table 1
High surface area NiO–Ni precursor screening

Precursor	State	Calcination	BET (m^2/g)	Yield (mg)	Theory (NiO) (mg)
500 mg $Ni(OH)_2$	Grn dry pwd	300 °C/4 h	140	393	403
		275 °C/4 h	171	390	403
		250 °C/4 h	177	398	403
500 mg Ni carbonate	Grn dry pwd	300 °C/4 h	141	310	315
500 mg Ni acetate	Grn dry pwd	300 °C/4 h	104	152	
500 mg Ni hydroxyacetate		300 °C/4 h	173	180	179
555 mg Ni hydroxyacetate		300 °C/1 h	72	382	199
	Recalcined	300 °C/1 h	240	249	199
	Recalcined	300 °C/0.5 h	267	194	199
500 mg Ni hydroxyacetate		275 °C/4 h	197	237	179
	Recalcined	275 °C/2 h	227	191	179
	Recalcined	275 °C/2 h	260	177	179
500 mg Ni formate	Grn dry pwd	300 °C/4 h	10	169	202
500 mg Ni citrate	Grn dry pwd	300 °C/4 h	216	138	
500 mg Ni lactate	Grn dry pwd	300 °C/4 h	135	120	121
500 mg Ni oxalate	Bluish dry pwd	325 °C/2 h	410	204	204
500 mg Ni oxalate	Bluish dry pwd	325 °C/1 h		No decomposition, still bluish	
	Recalcined	325 °C/0.5 h		Partial decomposition, partly black	
	Recalcined	325 °C/0.5 h	414	216	204
200 mg Ni dimethylglyoxime	Red pwd	300 °C/4 h	112	43	
400 mg Ni dimethylglyoxime	Red pwd	280 °C/4 h	33	99	
500 mg Ni dimethylglyoxime	Red pwd	260 °C/4 h	6	145	
500 mg Ni dimethylglyoxime	Red pwd	320 °C/4 h	66	106	
700 mg Ni oxalate	Bluish pwd	310 °C/6 h	273	389	286
	Recalcined	325 °C/2 h	382	296	

Ni hydroxide = $Ni(OH)_2$ Alfa 12517 FW92.72
Ni carbonate = $NiCO_3$ Alfa 22897 FW118.72
Ni acetate = $Ni(OOCCH_3)_2 \cdot xH_2O$ Alfa 12223
Ni hydroxyacetate $Ni(OOCCH_2OH)_2$ Alfa 39456 FW208.75
Ni formate = $Ni(OOCH)_2 \cdot 2H_2O$ Alfa 13801 FW184.77
Ni citrate = $Ni_3(C_6H_5O_7)_2 \cdot xH_2O$ Alfa 39634
Ni lactate = $Ni(OOCCHOHCH_3)_2 \cdot 4H_2O$ Alfa B23643 FW308.91
Ni oxalate = $NiC_2O_4 \cdot 2H_2O$ Alfa 39454 FW 182.76
Ni dimethylglyoxime = $Ni(C_4H_7N_2O_2)_2$ Alfa 39458 FW288.94

Thermal decomposition of the dry powder (as supplied by Alfa). Standard temperature ramp: 45 °C/4 h ramp/120 °C/4 h hold/2 h ramp/300 °C/4 h hold.

hydrogenation of octene under the reaction conditions $T = 55\ ^\circ\mathrm{C}$, $m(\mathrm{cat}) = 300$ mg, $V(C_8H_{16}) = 1.5$ ml, $V(CH_3OH) = 50$ ml.

3. Results

Some representative results for Ni, Fe, Rare Earth as well as Co-based mixed oxides will be presented below.

3.1. Results for nickel – Ni precursor screening – dry decomposition

Combustion synthesis has already been applied to Ni oxide but only low surface areas <100 m^2/g have been reported ([22] and references therein). Commercially available NiO nanopowder (Alfa 44297, 0.008–0.01 μm APS powder) had a BET surface area of 83.6 m^2/g (as supplied, no pretreatment, no outgassing) or 87.2 m^2/g (outgassed at 250 °C overnight). Commercial micronsized NiO (Aldrich 24,403-1; <10 μm particles) had a BET surface area of 31 m^2/g (as supplied).

We have investigated the thermal decomposition of dry powders of Ni salts that are convertible into the oxide upon air calcinations. As seen from Table 1, high surface areas >400 m^2/g are possible by dry decomposition of Ni oxalate while Ni citrate and Ni hydroxyacetate can achieve surface areas >200 m^2/g.

Theoretical yields, when starting from 500 mg Ni hydroxide $Ni(OH)_2$ as precursor, are 403 mg for NiO or 316 mg for (metallic) Ni. Mass balances are seen to be almost closed in most cases when assuming NiO as final product with roughly 0.1–2% residual carbon left over from incomplete combustion of the organic counteranion.

3.2. Results for nickel—acid screening

While dry powder decomposition only allows the synthesis of monometallic NiO, it is most desirable for catalytic applications to prepare well mixed multimetal oxides. Therefore, we resorted to wet combustion synthesis starting from an aqueous solution of dissolved metal salts in a combustible organic acid.

For the modification of the traditional Pechini (citric acid combustion) method, our strategy was based on the selection of low molecular weight and easy to decompose multifunctional carboxylic acids such as diacids, hydroxoacids and ketoacids (as a replacement for the traditional citric acid) to (a) solubilize the metal precursors by forming metal carboxalte solutions and (b) to allow for low calcination temperatures to burn off the organics without inducing sintering of the fresh metal oxide surfaces formed.

Table 2
High surface area NiO–organic acid screening

Acid	Calcinations (°C)	BET (m^2/g)
Glyoxylic	290	337
Glyoxylic	300	378
Glyoxylic	325	269
Diglycolic	325	245
Tartaric	325	205
Oxamic	325	189
Oxalic	325	185
Citric	325	153
Malic	325	149
Lactic	325	108
Malonic	325	99
Ketoglutaric	350	200
Malic	350	196
Tartaric	350	184
Glutaric	350	168
Succinic	350	146
Ketoglutaric	375	119
Ketoglutaric	400	105

Table 2 summarizes screening results for various acids whereby only calcinations temperature (but not calcinations time which was fixed to 4 h in air) and acid amount have been varied without a global optimization of the full parameter space (which will be addressed later). Table 2 identifies glyoxylic acid as the most suitable dispersant in the low temperature calcinations regime 290–310 °C with surface areas >350 m^2/g whereas ketoglutaric acid requires higher calcination temperatures in the range 350–400 °C to burn off coke.

3.3. Results for nickel—glyoxylic acid

Table 3 gives an overview of NiO samples prepared by the novel proposed glyoxylic acid method starting from Ni hydroxide as precursor. A clear green solution is formed upon gentle heating of Ni hydroxide in aqueous glyoxylic acid. The aqueous Ni glyoxylate solution thus formed is stable for at least 1 year. Ni hydroxide was the best precursor and superior to Ni acetate for highest surface areas to be achieved, while results with Ni nitrate were poor. We preferred Ni hydroxide over the carbonate or hydroxicarbonate because of the excessive foaming and gas evolution (coming along with spillover) of the latter ones when coming into contact with the

Table 3
High surface area NiO by glyoxylic acid method

500 mg $Ni(OH)_2$ + dispersant	Aging	State	Calcinations	BET (m^2/g)	Yield (mg)
10 ml 6.25% glyoxylic	None	Foggy soln	300 °C/3 h	337	460
		Recalcined	300 °C/0.5 h	331	403
10 ml 12.5% glyoxylic	None	Grn soln	300 °C/3 h	279	440
		Recalcined	300 °C/0.5 h	298	390
1 g $Ni(OH)_2$ + dispersant	Aging	State	Calcinations	BET (m^2/g)	Yield (mg)
10 ml 12.5% glyoxylic	None	Grn soln	320 °C/4 h	299	835
13 ml 10% glyoxylic	None	Grn soln	320 °C/4 h	310	829
14 ml 10% glyoxylic	None	Grn soln	320 °C/4 h	312	837
10 ml 15% glyoxylic	None	Grn soln	320 °C/4 h	338	847
12 ml 12.5% glyoxylic	None	Grn soln	320 °C/4 h	324	851
10 ml 15% glyoxylic	None	Grn soln	320 °C/4 h	325	862
12 ml 12.5% glyoxylic	None	Grn soln	320 °C/4 h	326	845
7 ml 20% glyoxylic	None	Grn soln	320 °C/4 h	327	836
7 ml 20% glyoxylic	None	Grn soln	315 °C/4 h	327	865

Standard temperature ramp: 45 °C/4 h ramp/120 °C/4 h hold/2 h ramp/300 °C/3 h hold (theoretical yield is 403 mg NiO from 500 mg $Ni(OH)_2$).

Table 4
High surface area Ni mixed oxides by wet combustion synthesis

Precursor	Dispersant	Aging for	State	Calcination	BET (m^2/g)	Yield (mg)
0.5 g $Ni(OH)_2$ + 100 mg $Mn(OAc)_2$ (93 Ni:7 Mn)	7 ml 3 M ketoglutaric	3 weeks	Grn gel/foam	350 °C/4 h	149	427
1 g $Ni(OH)_2$ + 100 mg $Mn(OAc)_2$ (96 Ni:4 Mn)	15 ml 3 M ketoglutaric	3 weeks	Grn gel/foam	350 °C/4 h	170	863
			Recalcined	400 °C/4 h	136	858
			Recalcined	450 °C/4 h	111	843
			Recalcined	500 °C/4 h	76	836
500 mg $Ni(OH)_2$ + 200 mg $Fe(OAc)_2$	6 ml 10% glyoxylic	None	Grn solution	300 °C/4 h	404	
1 g $Ni(OH)_2$ + 65 mg $Mn(OAc)_2$ + 100 mg $(NH_4)_2Pd(C_2O_4)_2{\cdot}2H_2O$	7 ml 20% glyoxylic	None	Grn solution	315 °C/4 h	326	
1 g $Ni(OH)_2$ + 6.5 ml 20% glyoxylic + 100 mg $(NH_4)_2Pd(C_2O_4)_2{\cdot}2H_2O$	80 mg $Ce(OAc)_3$	None	Grn solution	320 °C/4 h	321	
	160 mg $Cr(OAc)_3$	None	Grn solution	320 °C/4 h	334	
	150 mg $Al(OAc)_3$	None	Grn solution	320 °C/4 h	352	

acid. When aging the Ni glyoxylate solutions (i.e. evaporating water solvent) for a couple of weeks in open vials at room temperature in the hood, volume shrinkage by a factor of about 10 occurred and a transparent glassy green gel was formed, however, we found no difference as far as surface area of the calcined NiO is concerned when calcining the aged gel or directly drying/calcining the solution.

We used inexpensive and common precursors selected from only a handful of compounds (nitrates, hydroxides, carbonates, acetates, oxalates, acac). Best results for the Pechini method (which are reported in the tables) were achieved with hydroxides and carbonates, i.e. when starting from the metal carboxylates. Dry decomposition of solid Ni glyoxylate or Ni oxalate also works well while the (dry or wet) decomposition of Ni nitrate only gives poor results.

3.4. Results for mixed nickel systems

The proposed modified Pechini method is most powerful for the synthesis of mixed oxides and superior to other methods such as precipitation (difficult to achieve intimate mixing for many metals simultaneously) or dry decomposition (suitable only for monometallic oxides). The metals are entrapped and immobilized in the gel or polymeric resin that the acid turns into upon evaporating the solvent (water) when drying and/or calcining the solution. Table 4 gives examples of the binaries Ni–Mn and Ni–Fe oxides.

3.5. Characterization of high surface area Ni oxide

XRD identifies NiO as the major phase, possibly contaminated with very minor contributions of metallic Ni particles or Ni_2O_3 (Fig. 2, glyoxylic acid prep). Chemical analysis showed a residual carbon content of approximately 0.5% that helps stabilizing the oxidic matrix against sintering.

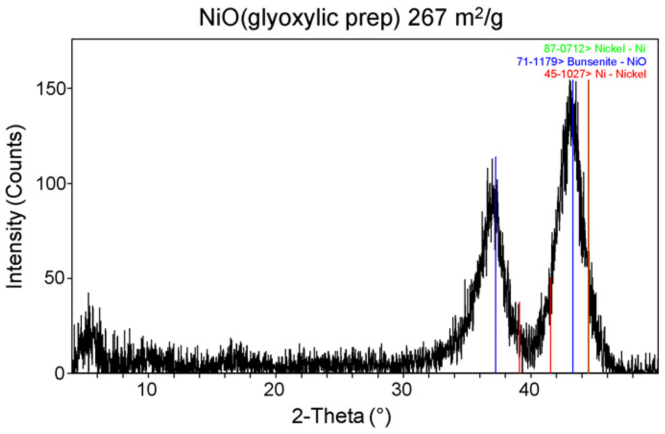


Fig. 2. XRD of high surface area NiO prepared by combustion synthesis with glyoxylic acid as dispersant.

3.6. Catalytic application of high surface area Ni oxides

Fig. 3 compares the hydrogenation activity of Ni–Ce–Pd with Raney-Ni (supplied from Fluka) for the slurry phase hydrogenation of octene to octane. Ce has been incorporated into the NiO matrix as stabilizer against sintering and traces of Pd allow to lower to reduction temperature of NiO to about 250 °C (gas phase H_2 reduction of NiO to Ni prior to feeding the octene reactant). It is seen that the doped Ni oxides (after careful reduction) are competitive to commercial Raney-Ni with respect to hydrogenation activity.

Although we report the catalytic activity only for Ni-Ce-Pd as a representative example, many more Ni samples (with W, Co, Mn, Fe, Cr, Al, Ce, Nb, Mo as binders and various Pd precursors for the promoter) were screened with similar results, i.e. many samples were competitive to Raney-Ni in octene hydrogenation. Ni loadings for all doped Ni samples are similar (above 90%) because the binder and promoters add up to only a few percent of the material.

3.7. Results for Rare Earth oxides

The synthesis of high surface area Rare Earth oxides has been attempted by all three methods (dry and wet combustion as well as precipitation). In the following we will be presenting representative results for holmium oxide. For commercially available Ho oxide nanopowder (as supplied by Aldrich 637327) we measured a BET of 14.5 m^2/g.

The rationale behind the design of the experiments was to screen the commonly available precursors and identify the best dispersant and calcination conditions for each precursor. No mathematical algorithm or evolutional techniques have been applied.

3.8. Results for holmium—dry decomposition

Table 5 summarizes results obtained by calcinations of dry powder precursors. Ho oxide substantially free of carbon is pink whereas brown or black material is indicative of larger amounts of residual coke. It is seen that BET >100 m^2/g is easily possible by calcination of Ho acetate whereas poor results are obtained for Ho carbonate as precursor.

Holmium acetate gives higher surface areas than the carbonate because Ho belongs to the block of RE metals which form infusible acetates (Dy, Ho, Er, Tm) where much higher surface areas are obtained than for the other RE (except cerium where high surface areas are also possible). The decomposition of the Dy, Ho, Er, Tm

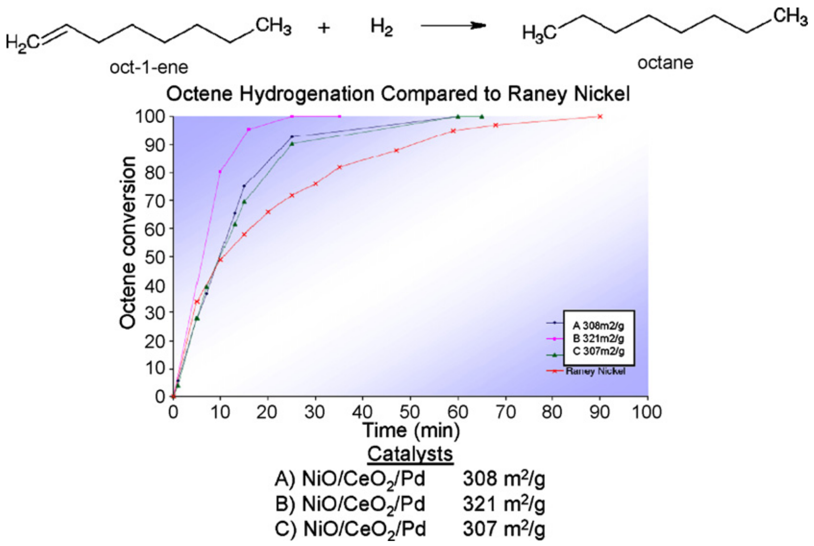


Fig. 3. Conversion vs. reaction time for the slurry phase catalytic hydrogenation of octene to octane over (pre-reduced) high surface area Ni-Ce-Pd catalysts (Ce content in the range from 1 to 6 wt%, Pd content from 0.02 to 0.2 wt%) compared to Raney-Ni. Reaction conditions: $T = 55\ ^\circ C$, $m(\text{cat}) = 300$ mg, $V(C_8H_{16}) = 1.5$ ml, $V(CH_3OH) = 50$ ml.

acetates is believed to directly yield the oxides without passing through the carbonate intermediate which is very stable (recall that the RE are basic) and therefore difficult to decompose and require higher calcinations temperatures resulting in lower surface areas. For RE metals other than the block of infusible acetates, only moderate surface areas are obtained (by dry decomposition) regardless of the precursor (carbonate, acetate, oxalate, acac) because the precursor is decomposed into the carbonate which releases CO_2 only at elevated temperature due to the basic nature of the metal (recall the extreme thermal stability of alkaline earth of La carbonate).

3.9. *Results for holmium—combustion synthesis*

Table 6 summarizes some results for broad acid screening as well as parameter optimization for the best acids identified (malonic, glutaric, succinic). It is seen that neither the traditional Pechini acids (citric, tartaric, malic) nor the novel ones (glyoxylic, ketoglutaric or diglycolic that gave superior results for Ni, Co, Fe, Mn, In, Sn) work well for Ho (and the other Rare Earths) resulting in brown material (i.e. require higher calcination temperatures for complete burn off of coke accompanied by surface area losses) whereas the simple diacids malonic, glutaric, succinic were found to work best resulting in pink (i.e. carbon-free) material already at relatively low calcination temperatures below 400 °C and decent surface areas in the range 80–120 m²/g. Fine tuning of acid/metal ratio and calcinations conditions are required for best results (highest surface areas).

For the combustion synthesis of Ho oxides, the carbonate was used as precursor (rather than the acetate which resulted in highest surface areas upon dry decomposition, see above) due to the easy and complete reaction with the organic acid whereby CO_2

Table 5
Holmium oxide by dry decomposition

Precursor	Dispersant	State	Calcination	BET (m²/g)	Yield
939 mg Ho acetate	None	Pink pwd	325 °C/4 h	133.5	520 mg pink
1.1 g Ho acetate	None	Pink pwd	335 °C/4 h	131.1	616 mg pink
1.17 g Ho acetate	None	Pink pwd	350 °C/4 h	133.0	640 mg pink
1.026 g Ho acetate	None	Pink pwd	375 °C/4 h	119.0	562 mg pink
1.01 g Ho acetate	None	Pink pwd	400 °C/4 h	113.8	545 mg pink
1.1 g Ho acetate	None	Pink pwd	450 °C/4 h	98.8	581 mg pink
807 mg Ho acetate	None	Pink pwd	500 °C/4 h	70.1	400 mg pink
970 mg Ho acetate	None	Pink pwd	360 °C/2 h	140.6	533 mg pink
969 mg Ho acetate	None	Pink pwd	350 °C/2 h	137.6	550 mg pink
		Recalcined	350 °C/1 h	136.8	528 mg pink
988 mg Ho acetate	None	Pink pwd	370 °C/1 h	125.0	565 mg pink
866 mg Ho acetate	None	Pink pwd	275 °C/4 h	133.2	487 mg pink
904 mg Ho acetate	None	Pink pwd	300 °C/4 h	134.0	499 mg pink
836 mg Ho carbonate	None	Pink pwd	350 °C/4 h	26.9	433 mg pink
1 g Ho carbonate	None	Pink pwd	350 °C/4 h	31.0	517 mg pink
1 g Ho carbonate	None	Pink pwd	375 °C/4 h	26.5	513 mg pink
1 g Ho carbonate	None	Pink pwd	375 °C/4 h	41.5	463 mg pink
1 g Ho carbonate	None	Pink pwd	400 °C/4 h	37.2	494 mg pink
1 g Ho carbonate	None	Pink pwd	425 °C/4 h	40.7	474 mg pink
1 g Ho carbonate	None	Pink pwd	450 °C/4 h	44.3	461 mg pink
1 g Ho carbonate	None	Pink pwd	500 °C/4 h	39.7	460 mg pink

Temperature ramp: 55 °C/1 h ramp/120 °C/1 h hold/1 h ramp/400 °C/4 h hold in 40 ml vial.

Table 6
Ho oxide by wet combustion synthesis

Precursor	Dispersant	State	Calcination	BET (m^2/g)	Yield
1 g Ho carbonate	3 ml H_2O + 2 ml 12.5% glyoxylic				
		Pink soln	375 °C/4 h	25.2	478 mg brown
		Recalcined	400 °C/4 h	20.8	461 mg brown
		Recalcined	425 °C/4 h	22.8	459 mg brown
		Recalcined	425 °C/4 h	32.1	442 mg pink
		Recalcined	425 °C/4 h	35.2	429 mg pink
		Recalcined	425 °C/4 h	35.0	429 mg pink
1 g Ho carbonate	5 ml 1 M tartaric	Pink slurry	375 °C/4 h	27.9	491 mg brown
		Recalcined	400 °C/4 h	13.8	474 mg brown
1 g Ho carbonate	7.5 ml 1 M malic	Pink slurry	375 °C/4 h	20.4	491 mg brown
		Recalcined	400 °C/4 h	13.5	481 mg brown
1 g Ho carbonate	10 ml H_2O + 600 μl pyruvic				
		Pink soln	375 °C/4 h	19.3	484 mg brown
		Recalcined	400 °C/4 h	8.9	478 mg brown
1 g Ho carbonate	10 ml H_2O + 500 mg diglycolic				
		Pink slurry	375 °C/4 h	18.9	473 mg brown
		Recalcined	400 °C/4 h	9.9	468 mg brown
1 g Ho carbonate	10 ml H_2O + 500 mg ketoglutaric				
		Pink slurry	375 °C/4 h	34.1	468 mg pink
		Recalcined	400 °C/4 h	35.7	454 mg pink
1 g Ho carbonate	10 ml H_2O + 1 g ketoglutaric				
		Pink slurry	375 °C/4 h	17.6	472 mg pink
		Recalcined	400 °C/4 h	18.5	465 mg pink
1 g Ho carbonate	10 ml H_2O + 500 μl 70% Glycolic				
		Pink slurry	375 °C/4 h	20.0	592 mg brown
		Recalcined	400 °C/4 h	3.9	513 mg brown
1 g Ho carbonate	10 ml 1 M lactic	Pink slurry	375 °C/4 h	7.7	437 mg brown
		Recalcined	400 °C/4 h	6.5	478 mg brown
1 g Ho carbonate	10 ml 0.5 M oxamic	Pink slurry	375 °C/4 h	20.2	493 mg brown
		Recalcined	400 °C/4 h	13.4	488 mg brown
1 g Ho carbonate	5 ml 1 M glutaric	Pink slurry	375 °C/4 h	77.7	466 mg pink
		Recalcined	400 °C/4 h	65.8	437 mg pink
1 g Ho carbonate	5 ml 1 M glutaric	Pink slurry	350 °C/4 h	81.7	471 mg pink
		Recalcined	360 °C/4 h	79.0	458 mg pink
1 g Ho carbonate	10 ml H_2O + 500 mg *trans*-aconitic				
		Pink slurry	375 °C/4 h	15.7	502 mg brown
		Recalcined	400 °C/4 h	11.9	492 mg brown
		Recalcined	425 °C/4 h	11.9	479 mg brown
1 g Ho carbonate	5 ml 1 M citric	Pink slurry	375 °C/4 h	39.0	485 mg brown
		Recalcined	400 °C/4 h	21.8	464 mg brown
		Recalcined	425 °C/4 h	18.1	449 mg brown
1 g Ho carbonate	5 ml 1 M malonic	Pink slurry	375 °C/4 h	41.9	440 mg pink
		Recalcined	400 °C/4 h	24.8	457 mg pink
		Recalcined	425 °C/4 h	20.9	452 mg pink
1 g Ho carbonate	10 ml H_2O + 500 mg glycine				
		Pink slurry	375 °C/4 h	18.8	515 mg brown
		Recalcined	400 °C/4 h	11.3	492 mg brown
		Recalcined	425 °C/4 h	9.7	484 mg yellowish
1 g Ho carbonate	10 ml H_2O + 500 μl pyruvic				
		Pink soln	375 °C/4 h	6.4	498 mg brown
		Recalcined	400 °C/4 h	6.4	484 mg brown
		Recalcined	425 °C/4 h	6.2	476 mg brown
1 g Ho carbonate	5 ml H_2O + 5 ml 25% gluconic				
		Pink soln	375 °C/4 h	33.2	497 mg brown
		Recalcined	400 °C/4 h	29.7	488 mg brown
		Recalcined	425 °C/4 h	23.1	469 mg pink
1 g Ho carbonate	4 ml 2 M tartaric	Pink slurry	375 °C/4 h	40.3	489 mg brown
		Recalcined	390 °C/4 h	35.4	482 mg brown
1 g Ho carbonate	6 ml 1 M glutaric	Pink slurry	375 °C/4 h	85.5	470 mg pink
		Recalcined	375 °C/2 h	81.6	454 mg pink
1 g Ho carbonate	7 ml 1 M glutaric	Pink slurry	375 °C/4 h	87.0	473 mg pink
		Recalcined	375 °C/2 h	83.4	464 mg pink

Table 6 (*Continued*)

Precursor	Dispersant	State	Calcination	BET (m^2/g)	Yield
1 g Ho carbonate	8 ml 1 M glutaric	Pink slurry	375 °C/4 h	86.2	473 mg pink
		Recalcined	375 °C/2 h	83.1	462 mg pink
1 g Ho carbonate	4 ml 2 M glutaric	Pink slurry	375 °C/4 h	87.4	478 mg pink
1 g Ho carbonate	2 ml 4 M glutaric	Pink slurry	375 °C/4 h	86.8	476 mg pink
1 g Ho carbonate	8 ml 1 M malonic	Pink slurry	375 °C/4 h	82.8	407 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	375 °C/4 h	81.3	404 mg pink foam
1 g Ho carbonate	4 ml 1 M malonic	Pink slurry	360 °C/4 h	17.0	499 mg pink-brown
		Recalcined	375 °C/4 h	15.3	489 mg pink-brown
1 g Ho carbonate	5 ml 1 M malonic	Pink slurry	360 °C/4 h	18.0	493 mg pink-brown
		Recalcined	375 °C/4 h	15.8	488 mg pink-brown
1 g Ho carbonate	10 ml H_2O + 500 mg succinic				
		Pink slurry	375 °C/4 h	15.2	472 mg brown
		Recalcined	400 °C/4 h	11.3	470 mg brown
1 g Ho carbonate	10 ml H_2O + 750 mg succinic				
		Pink slurry	375 °C/4 h	67.5	464 mg pink
		Recalcined	400 °C/4 h	59.4	443 mg pink
1 g Ho carbonate	10 ml H_2O + 1g succinic				
		Pink slurry	375 °C/4 h	70.4	479 mg pink
1 g Ho carbonate	10 ml H_2O + 2g ketoglutaric				
		Pink soln	375 °C/4 h	17.3	380 mg pink
		Recalcined	400 °C/4 h	17.0	377 mg pink
1 g Ho carbonate	5 ml H_2O + 500 μl methoxyacetic				
		Pink slurry	375 °C/4 h	8.4	504 mg brown
		Recalcined	400 °C/4 h	7.1	486 mg brown
1 g Ho carbonate	5 ml H_2O + 1 ml methoxyacetic				
		Pink slurry	375 °C/4 h	10.5	498 mg brown
		Recalcined	400 °C/4 h	7.5	476 mg brown
1 g Ho carbonate	10 ml H_2O + 2 g diglycolic				
		Pink slurry	375 °C/4 h	9.1	500 mg brown
		Recalcined	400 °C/4 h	8.6	498 mg brown
1 g Ho carbonate	7 ml 10% oxalic	Pink slurry	375 °C/4 h	28.4	481 mg brown
1 g Ho carbonate	9 ml 10% oxalic	Pink slurry	375 °C/4 h	27.3	483 mg brown
1 g Ho carbonate	7 ml 10% oxalic	Pink slurry	400 °C/4 h	44.9	486 mg brown
		Recalcined	425 °C/4 h	29.8	479 mg pink
1 g Ho carbonate	8 ml 1 M malonic	Pink slurry	360 °C/4 h	83.6	403 mg pink foam
1 g Ho carbonate	8 ml 1 M malonic	Pink slurry	350 °C/4 h	87.3	408 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	340 °C/4 h	93.9	411 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	330 °C/4 h	96.5	420 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	320 °C/4 h	98.9	426 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	290 °C/5 h	110.9	440 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	280 °C/6 h	112.9	428 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	270 °C/8 h	113.5	430 mg pink foam
1 g Ho carbonate	7 ml 1 M malonic	Pink slurry	300 °C/3 h	110.0	415 mg pink foam
1 g Ho carbonate	6 ml 1 M malonic	Pink slurry	300 °C/6 h	51.4	452 mg pink foam
1 g Ho carbonate	3 ml 3 M citric	Pink slurry	350 °C/4 h	11.0	510 mg brown
		Recalcined	375 °C/4 h	11.6	494 mg brown
		Recalcined	400 °C/2 h	11.3	487 mg brown

Temperature ramp: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/375 °C/4 h hold in 40 ml vial.

is released and the metal carboxylate is formed in situ. Generally we found higher surface areas for the metal carbonate or hydroxide precursors because no additional counter radical (acetate, oxalate) would have to be removed upon calcinations. The nitrates generally showed poor performance. In other words, the choice of precursor depends on the synthetic method and is certainly one of the parameters to be optimized.

3.10. Results for holmium—precipitation

Table 7 summarizes precipitation results for 3 different Ho precursors (acetate, chloride, nitrate) that were pumped at 78 °C into excess NMe_4OH base. We prefer pH titration over precipitation at constant pH because previous scouting experiments showed high surface areas were easy to achieve by pH titration without elaborate optimization and precise adjustment of pH. It is seen from Table 7 that Ho oxides of about 100 m^2/g are possible by calcinations of the freshly precipitated hydroxide.

3.11. Summary rare earth oxides—general trends

The highest surface areas achieved for the different lanthanides and synthesis methods (precipitation, wet and dry combustion) are summarized in Table 8. With the exception of Ce (where precipitation was found to be far superior to combustion synthesis and CeO_2 >300 m^2/g could be produced), it is seen that precipitation can afford roughly about 100 m^2/g for any metal whereas (dry or wet) combustion gives inferior results for all Rare

Table 7
Ho oxide by precipitation

pH titration	T (°C)	Calcination	BET (m^2/g)	Yield (mg)
5 g $Ho(OAc)_3$ + 70 ml H_2O pumped into 50 ml 1 M NMe_4OH + 50 ml H_2O	78	400 °C/4 h	98.4	1317
		350 °C/4 h	100.7	1310
5.7 g $HoCl_3$ + 40 ml H_2O pumped into 50 ml 1N NMe_4OH + 50 ml H_2O	78	450 °C/4 h	84.8	1405
		550 °C/4 h	76.6	1405
5.78 g $HoCl_3$ + 40 ml H_2O pumped into 50 ml 1 M NMe_4OH + 50 ml H_2O	78	350 °C/4 h	100.7	1465
		400 °C/4 h	98.9	1448
13.5 ml 1.1269 M $Ho(NO_3)_3$ + 16.5 ml H_2O into 50 ml 1 M NMe_4OH + 50 ml H_2O	78	350 °C/4 h	90.9	1419
		400 °C/4 h	84.4	1432

Precipitation/pH titration in 250 ml three-neck flask; masterflex pH controller; peristaltic pump; isolation of ppt by centrifugation in two 40 ml vials; 4 wash steps in 40 ml vials. Temperature ramp: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/350 °C/4 h hold in 40 ml vial.

Table 8
Highest BET surface areas achieved by precipitation, dry or wet combustion synthesis for the Rare Earth oxides

Highest BET surface areas (m^2/g) achieved for Rare Earth oxides												
Dry decomposition												
Ce 168	Pr 23	Nd 33	Sm 32	Eu 27	Gd 33	Tb 52	Dy 122	Ho 141	Er 148	Tm 152	Yb 21	Lu 36
Precipitation												
Ce 306	Pr 120	Nd 114	Sm 80	Eu 72	Gd 64	Tb 88	Dy 84	Ho 101	Er 123	Tm 94	Yb 100	Lu 98
Combustion Synthesis (novel Pechini acids)												
Ce	Pr	Nd 58	Sm 103	Eu 26	Gd 65	Tb 54	Dy 114	Ho 114	Er 132	Tm	Yb	Lu

Earth besides the block of Dy, Ho, Er, Tm where surface areas higher than 100 m^2/g can be achieved by (dry or wet) combustion. It is recalled that dry and wet combustion are different (although a dry metal carboxylate may be formed by crystallization from the solution during drying) because the wet combustion method makes use of a non-stoichiometric acid/metal ratio (usually higher than 1, i.e. molar excess acid). Interestingly, superior results were obtained by dry decomposition of Dy, Ho, Er, Tm acetates only

Table 9
Synthesis of multimetal oxides by soft combustion synthesis

Composition of product (mol%)	Acid	Acid/metal ratio		Calcination		BET surface area (m^2/g)
		(mg/mmol)	(mmol/mmol)	Temperature (°C)	Time (h)	
Co47 In29 Ce24	Glyoxylic acid	417.4	4.5	300	4	134.4
Co47 In29 Ce24	Glyoxylic acid	208.7	2.3	300	4	140.7
Co47 In29 Ce24	Glyoxylic acid	104.4	1.1	300	4	141.3
Co48 Sb28 Ce24	Glyoxylic acid	420.2	4.6	300	4	132.9
Co48 Sb28 Ce24	Glyoxylic acid	210.1	2.3	300	4	125.1
Co48 Sb28 Ce24	Glyoxylic acid	105.1	1.1	300	4	73.3
Co14 In16 Ce70	Glyoxylic acid	150.5	1.6	300	4	150.4
Co14 Sb16 Ce70	Glyoxylic acid	151.0	1.6	300	4	137.7
Co13 Ge18 Ce69	Glyoxylic acid	147.6	1.6	300	4	159.3
Co13 Sn17 Ce70	Glyoxylic acid	149.7	1.6	300	4	161.0
Co13 Sn17 Y70	Glyoxylic acid	147.8	1.6	400	4	74.6
Co13 Sb16 Y71	Glyoxylic acid	149.1	1.6	400	4	69.8
Co13 In17 Y70	Glyoxylic acid	148.5	1.6	400	4	66.0
Co13 Ge18 Y69	Glyoxylic acid	145.8	1.6	400	4	48.3
Co13 Sn17 Y70	Ketoglutaric acid	118.2	0.8	400	4	148.8
Co13 Sn17 Y70	Ketoglutaric acid	236.5	1.6	400	4	145.9
Co13 Sn17 Y70	Ketoglutaric acid	354.7	2.4	400	4	148.8
Co13 Sn17 Y70	Oxalacetic acid	118.2	0.9	400	4	191.1
Co13 Sn17 Y70	Oxalacetic acid	236.5	1.8	400	4	83.7
Co13 Sn17 Y70	Oxalacetic acid	354.7	2.7	400	4	38.8
Co13 Sn17 Y70	Diglycolic acid	118.2	0.9	400	4	71.0
Co13 Sn17 Y70	Diglycolic acid	236.5	1.8	400	4	45.5
Co13 Sn17 Y70	Diglycolic acid	354.7	2.6	400	4	37.9
Co13 Sn17 Y70	Oxalacetic acid	70.9	0.5	400	4	199.8
Co13 Sn17 Y70	Oxalacetic acid	94.6	0.7	400	4	192.2
Co13 Sn17 Y70	Oxalacetic acid	141.9	1.1	400	4	180.9
Co7 Fe7 Sn16 Ce70	Glyoxylic acid	46.0	0.5	300	2	132.4
Co7 Fe7 Sn16 Ce70	Glyoxylic acid	138.1	1.5	300	2	156.3
Co7 Fe7 Sn16 Ce70	Glyoxylic acid	230.1	2.5	300	2	135.1
Co7 Fe7 Sn16 Ce70	Ketoglutaric acid	73.1	0.5	300	2	130.2
Co7 Fe7 Sn16 Ce70	Ketoglutaric acid	219.2	1.5	300	2	134.8
Co7 Fe7 Sn16 Ce70	Ketoglutaric acid	365.3	2.5	300	2	127.3

whereas the carbonates always resulted in low surface areas. On the other hand, for all other Rare Earth outside this favorable block of 4 metals, dry decomposition always led to poor results regardless of the metal precursor chosen (acetate, carbonate, acac). As far as wet combustion is concerned, best results were obtained with malonic or glutaric acid as dispersants, i.e. essentially carbon-free (yellowish, white or pink) material >100 m^2/g for Sm, Dy, Ho, Er. Traditional Pechini acids or the novel ones that proved to be well suited for many main group or transition metals (glyoxylic, ketoglutaric, oxalacetic, diglycolic) were less good for the Rare Earths.

3.12. Excerpt of results for higher dimensional multimetal oxides (example: Co systems)

We have previously synthezised a library of Ru–Co–Ce–Y quaternaries by the modified Pechini method using Ce(III) nitrate, Co(II) nitrate, Y(III) nitrate and Ru(III) nitrosyl nitrate as precursors in aqueous glyoxylic acid as dispersant and calcining the solution at 350 °C for 4 h in air [20]. Catalytic results for combined CO oxidation and VOC removal have been presented elsewhere [10,20,21]. We have then been investigating other mixed Co oxides for applications in other areas. Table 9 gives an excerpt of ternary and quaternary Co oxides prepared by soft combustion synthesis.

3.13. Summary—general trends

The highest surface areas achieved for the different synthesis methods (precipitation, wet and dry combustion) are summarized in Table 10. BET surface areas >100 m^2/g are possible for many metals using a variety of methods after calcination in the temperature range 300–500 °C [7,11].

Precipitation (of the hydroxides) was found to be far superior to combustion synthesis for La (145 m^2/g versus 45 m^2/g) and Ce (306 m^2/g versus 168 m^2/g) and most of the Rare Earth (except the Dy–Ho–Er–Tm block where wet as well as dry combustion resulted in the highest surface areas). Precipitation has not been applied by us to Ti and Zr where combustion synthesis gave poor results.

On the other hand, the modified Pechini method is well suited and resulted in surface areas >200 m^2/g for Ni, Co, Fe, Mn, Y, Sn and Nb. Best results have been obtained for glyoxylic acid, oxalacetic acid, and ketoglutaric acid.

Glyoxylic acid was found to work very well for Ni, Sn, In, Mn, Fe [8,9,12–14] and ketoglutaric was best for Co while oxalacetic gave high surface areas for yttria [15]. Interestingly, neither glyoxylic nor ketoglutaric produced high surface area Cu oxide but diglycolic was the best acid identified resulting in decent surface areas >80 m^2/g.

The proposed modified Pechini method did not work well for the traditional carrier materials Ti and Zr while for Nb glycolic proved to be superior to glyoxylic. For V and Mo, glyoxylic and oxalic gave similar results.

These novel Pechini acids have a low decomposition temperature in common, in the temperature range of 300–350 °C, thus allowing relatively low calcination temperatures and concomitant mitigation of surface sintering. These acids mostly decompose into volatiles (e.g. ketoglutaric acid → acetone + CO_2) and are less prone to coking. For instance, the isolated powders in the case of Sn, Ce, In are yellowish and in the case of Ho, Er pinkish with the mass balance almost closed thus indicating the absence of larger amounts of coke deposits. On the other hand, the high boiling traditional Pechini acids citric and malic yield black or brown materials when calcined <350 °C and would require temperatures of the order of 400 °C to burn off coke completely.

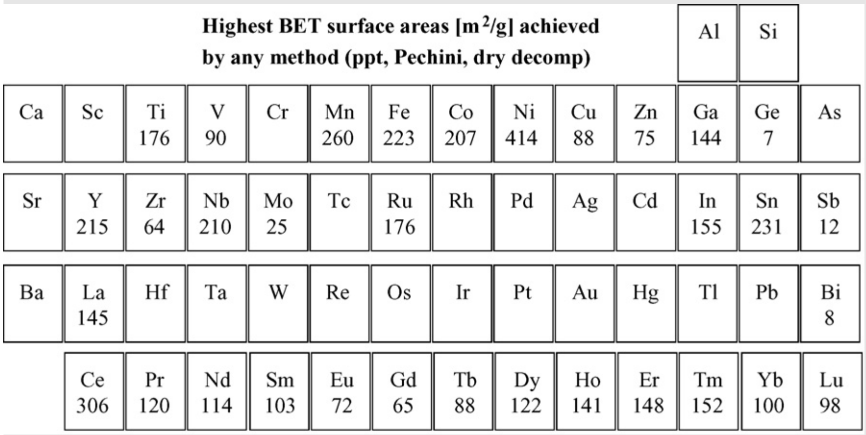
The solubility of, for instance, Sn(IV) acetate, In(III) acetate, Mn(II) acetate or Ni(II) hydroxide in aqueous glyoxylic acid is very high thus allowing high productivities (space-time-yields) and rendering the 'glyoxylic acid method' a convenient and flexible tool for the synthesis of these porous metal oxides. Moreover, as Table 9 reveals, mixed metal oxides with high surface areas can also be synthesized, even in the presence of (hard to stabilize) base metals (such as Co in Table 9).

The optimal calcination temperature is governed by the ability of the metal to form carbonates and their stability. The more acidic metals such as Ni, Co can be calcined at ~300 °C whereas Zn requires slightly higher temperature of ~325 °C to decompose Zn carbonate that might be formed as intermediate. The more basic Y has to be calcined at ~400 °C for carbonate decomposition.

For the strongly basic metals forming extremely stable carbonates upon combustion in the presence of organics (La), one has to resort to precipitation (by hydroxide bases) when high surface areas are wanted.

For ceria, precipitation resulted in far higher surface areas >300 m^2/g than combustion synthesis [11,18]. For the remaining Rare Earth metals poor results are usually obtained by combustion due to the high stability of the carbonates (as precursors or intermediates) with the exception of Dy–Ho–Er–Tm when decomposing their non-fusable acetates or slurrying their carbonates into aqueous malonic or glutaric acid [16].

Table 10
Highest BET surface areas achieved by precipitation, dry or wet combustion synthesis for metal oxides



Highest BET surface areas [m^2/g] achieved by any method (ppt, Pechini, dry decomp)

											Al	Si	
Ca	Sc	Ti 176	V 90	Cr	Mn 260	Fe 223	Co 207	Ni 414	Cu 88	Zn 75	Ga 144	Ge 7	As
Sr	Y 215	Zr 64	Nb 210	Mo 25	Tc	Ru 176	Rh	Pd	Ag	Cd	In 155	Sn 231	Sb 12
Ba	La 145	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi 8
	Ce 306	Pr 120	Nd 114	Sm 103	Eu 72	Gd 65	Tb 88	Dy 122	Ho 141	Er 148	Tm 152	Yb 100	Lu 98

As far as the noble metals are concerned, high surface area oxides >180 m^2/g could only be produced for Ru (e.g. from Ru nitrosyl acetate and ketoglutaric acid) while the other precious metals got reduced by the organic acid to the metal (i.e. metallic state) upon mild heating already. Interestingly, for Ce and Ru, even the chloride precursors gave decent surface areas, possibly by in situ Deacon oxidation of residual chloride during calcination in air.

4. Discussion

A variety of synthesis techniques have been used to prepare metal oxide materials. The most common techniques include conventional precipitation, the Pechini, or citric acid combustion process, and a variety of sol–gel techniques. Typical precipitation methods utilize stable, acidic metal salts in solution. The solution is combined with a base that increases the pH of the metal salt solution and destabilizes the metal salts to form metal hydroxides and/or metal carbonates that precipitate out of the solution. This reaction results in counter-anions of the metal salt, such as nitrates or chlorides, and the counter-cations of the base, such as Na, K, or NH_4 being present. After the precipitation, it is usually desirable to remove the ions from the base and the salt by washing, usually with a solvent such as water. However, this does not typically remove all of the impurities.

In order to avoid the ion contamination issue, precipitation with urea or hydrazine (which both decompose into volatiles upon boiling the solution) have been found to give comparable results to the use of other bases, such as NaOH or Na_2CO_3 [12,23,24]. Hydrazine or urea can be advantageous, since the precipitation agent is almost completely removed leaving little or no counter-cations. Hydrazine decomposes upon boiling into nitrogen, hydrogen and water, and the anion of the metal precursor (such as a chloride) is also removed from the system as a volatile gas, such as HCl. Urea breaks down to ammonia and CO_2 with the ammonia released being the actual base/precipitation agent thus forming NH_4Cl or NH_4NO_3 salts that may partly evaporate and partly reside in the solution. The solutions have to be heated to about 90 °C or refluxed during precipitation and aging thus adding to the energy cost.

The Pechini, or citrate method [1–6], involves combining a metal precursor with water, citric acid and a polyhydroxyalcohol, such as ethylene glycol. The components are combined into a solution which is then heated to remove the water. A viscous oil remains after heating. The oil is then heated to a temperature that polymerizes the citric acid and ethyleneglycol by polycondensation, resulting in a solid resin. The resin is a matrix of the metal atoms bonded through oxygen to the organic radicals in a cross-linked network. The resin is then calcined at a temperature typically above 500 °C to burn off the polymer matrix, leaving a porous metal oxide. The Pechini method is advantageous in that it utilizes components that are inexpensive and easy to handle. However, the method results in materials having BET surface areas substantially lower than those materials created using precipitation and sol–gel methods.

Typical sol–gel methods utilize metal alkoxide precursors in organic solvents with an aqueous inorganic acid, such as nitric acid or hydrochloric acid. The inorganic acid acts as a catalyst allowing the water to hydrolyze the metal alkoxide bonds in a hydrolysis reaction by protonation, forming a metal hydroxide and an alcohol. Subsequent condensation reactions involving the metal hydroxide units reacting with other metal hydroxide units or remaining metal alkoxides result in the metal molecules bridging, and water and alcohol being created. As the number of bridged metal molecules increases, agglomeration occurs, forming irregular agglomerates and eventually growing into a three-dimensional amorphous polymer network, or a gel. The remaining water and alcohol, which is a neutral non-ionic unreactive organic solvent, is evaporated from the system leaving little to no traces of the former metal counter-anion behind. The gel is then calcined, resulting in a porous, solid metal oxide. While the current sol–gel processes produce porous metal oxide materials having surface areas superior to those produced by precipitation and the Pechini method, the method suffers from the alkoxide precursors being expensive, flammable, viscous and difficult and dangerous to handle.

As can be seen from summary Table 10, high surface areas >100 m^2/g are possible for many metal oxides and mixtures by precipitation, dry decomposition as well as Pechini and related methods. The various synthesis methods we have developed complement each other with respect to achievable surface area/porosity and residual contaminations, in particular:

Synthesis method	Advantage	Disadvantage
Precipitation	High surface area	Possibly Na, K, Cl contamination; metal losses
Dry decomposition	Easy and inexpensive	Monometallic oxides only
Pechini method	Flexible; mixed metal oxide synthesis	Residual carbon contamination

When screening alternative Pechini acids (different from citric and malic) we discovered that significant surface area gains for many main group and transition metal oxides can be realized by resorting to organic acids such as glyoxylic, ketoglutaric or oxalacetic acid that are easily decomposable at low calcination temperatures in the range 300–350 °C without concomitant formation of refractory coke. For the Rare Earth oxides, malonic acid and glutaric acid were identified as the best dispersants for Dy–Ho–Er–Tm (i.e. the block of non-fusable lanthanide acetates) with calcinations temperatures in the range 350–400 °C being optimal. Therefore, we propose a modification of the Pechini method using these novel acids as dispersants for the synthesis of fairly general classes of porous metal oxide as well as mixed metal oxides [7–18]. Often we observe gel formation when evaporating the solvent (either upon prolonged standing at room temperature or when heating up for drying). Whether the gel is composed of metal oxide bridges and/or a metal carboxylate network requires further investigation. Ketoglutaric acid, for instance, constantly decomposes (into acetone and CO_2) upon stirring thus resulting in high losses of acid from the system until pH has risen to a point where gelation occurs. However, the mass balance (for the dried gel or in case of a too low calcination temperature) indicates considerable residual organics in the gel that must be burned off during calcination. In summary, the proposed new method is as easy and flexible to carry out as the classical Pechini method but allows the very high surface areas to be achieved that are characteristic of a sol–gel process and advantageously utilizes common inorganic metal precursors (rather than alkoxides).

5. Conclusion

Over the past couple of years, we have synthesized several tens of thousands of samples on a gram scale by dry and wet combustion synthesis for various catalytic applications including high surface area carriers for WGS and emissions control (Ce, Y, Sn), solid acids (Nb), Fischer–Tropsch (Fe–Mn), hydrogenations (Ni), total and partial oxidations (Ru–Co, Mo–V), HDS and HDN (Ni–Co–Mo).

Many high surface area metal oxides are available by a novel modified Pechini method (all water based soft combustion synthesis) using aqueous solutions of thermally labile organic acids as dispersants for common inorganic metal precursors such as formate, acetate, acac, hydroxide, carbonate, and even chloride that are cheap, commercially available, non flammable and non-alkoxide precursors. The concept consists of selecting easy-to-decompose organic acids that allow low temperature calcinations thus preventing surface area loss by sintering. Glyoxylic, oxalacetic, and ketoglutaric acid decompose in the temperature range 300–350 °C into volatiles without excessive coking. Calcination temperature, acid/metal ratio, and net initial weight of metal precursor are the principal parameters for high surface areas to be achieved and must be carefully optimized in small increments. We have demonstrated that high surface areas are achievable by means of aqueous routes after careful optimization of synthesis parameters, without resorting to organic solvents, sol–gel, supercritical drying or templates/hydrothermal synthesis. Our combustion synthesis is also well suited for the preparation of mixed oxides from mixed metal solutions in aqueous organic acids. Productivity is high since concentrated metal solutions can be used and neither aging nor washing are required. High purity materials can be easily produced that are strictly free of Cl, Na, K by proper metal precursor selection and only contaminated by residual carbon.

The proposed modified Pechini or ‘‘glyoxylic acid combustion method’’ is generally applicable to the acidic metals while for the strongly basic metals (alkaline earth, La, Ce) precipitation of the hydroxides is to be preferred due to the initial transformation of metal carboxylates into the very stable carbonates intermediates the decomposition of which would require very high temperatures thus resulting in pronounced particle agglomeration by sintering. The Pechini method is ideally suitable for high throughput robotic synthesis of metal oxides and mixed metal oxides in particular.

References

[1] Z. Hui, P. Michele, J. Mater. Chem. 12 (2002) 3787–3791.

[2] B.L. Cushing, V.L. Kolesnichenko, C.J. O'Connor, Recent advances in the liquid phase syntheses of inorganic nanoparticles, Chem. Rev. 104 (2004) 3893–3946.

[3] M.P. Pechini, US 3,330,697, 1967.

[4] H.M. Reichenbach, P.J. McGinn, J. Mater. Res. 16 (4) (2001) 967.

[5] H.M. Reichenbach, P.J. McGinn, Appl. Catal. A 244 (2003) 101.

[6] US 6,372,686, US 6,352,955, US 5,977,017, US 5,939,354, US 2002/0042341, WO 97/37760 to Catalytic Solutions Inc.

[7] M. Schlichter, High Surface Area Metal Oxides, Diploma Thesis, Symyx Technologies, Santa Clara, 2005.

[8] A. Hagemeyer, et al., High surface area tin oxide catalyst carriers, in: 19th NAM Meeting, Philadelphia, PA, May 22–27, 2005.

[9] B. Smaka, et al., High surface area tin oxide catalyst carriers, in: 10th International Symposium on Catalyst Deactivation, Berlin, Germany, February 5–8, 2006.

[10] A. Hagemeyer, Z. Hogan, G. Streukens, H. Turner, A. Volpe, H. Weinberg, K. Yaccato, Novel Ru-Co catalysts for combined low temperature CO oxidation/VOC combustion, in: ACS Spring National Meeting, Atlanta, GA, March 26–30, 2006.

[11] WO 2006/119311 (assigned to Symyx Technologies, 2006).

[12] A. Hagemeyer, Z. Hogan, M. Schlichter, B. Smaka, G. Streukens, H. Turner, A. Volpe, H. Weinberg, K. Yaccato, Appl. Catal. A 317 (2007) 139–148.

[13] A. Hagemeyer, M. Schlichter, A. Volpe, High surface area manganese and iron oxides, in: ACS National Meeting, Chicago, IL, March 25–29, 2007.

[14] A. Hagemeyer, M. Schlichter, A. Volpe, High surface area indium oxide and indium–tin mixed oxide, in: AIChE Spring National Meeting, Houston, TX, April 22–26, 2007.

[15] A. Hagemeyer, M. Schlichter, A. Volpe, High surface area yttria, in: 20th NAM Meeting, Houston, TX, June 17–22, 2007.

[16] C. Fink, A. Hagemeyer, M. Schlichter, A. Volpe, High surface area rare earth oxides, in: EUROPACAT VIII Conference, Turku, Finland, August 26–31, 2007.

[17] A. Hagemeyer, Z. Hogan, C. Lugmair, M. Schlichter, A. Volpe, High surface area niobia, in: ACS National Meeting, Boston, MA, August 19–23, 2007.

[18] C. Fink, A. Hagemeyer, Z. Hogan, A. Volpe, J. Yoder, High surface area ceria, Appl. Catal. A, in preparation.

[19] C. Brooks, S. Cypes, R.K. Grasselli, A. Hagemeyer, Z. Hogan, A. Lesik, G. Streukens, A. Volpe, H. Turner, H. Weinberg, K. Yaccato, Top. Catal. 38 (1–3) (2006) 195–209.

[20] S. Cypes, A. Hagemeyer, Z. Hogan, A. Lesik, G. Streukens, A. Volpe, H. Weinberg, K. Yaccato, Triple function Ru catalysts for low-temperature CO oxidation, in: VOC Combustion and SCR-DeNOx, Paper P44313, Proceedings AIChE Annual Meeting, San Francisco, CA, November 12–17, 2006.

[21] S. Cypes, A. Hagemeyer, Z. Hogan, A. Lesik, G. Streukens, A.F. Volpe Jr., W.H. Weinberg, K. Yaccato, High throughput screening of low temperature CO oxidation catalysts using IR thermography, in: J. Margitfalvi (Ed.), Combinatorial Chemistry & High Throughput Screening CCHTS, Special Issue on Catalysis, in press.

[22] Y. Chang Kang, S. Bin Park, Y. Whan Kang, Nanostruct. Mater. 5 (7/8) (1995) 777–791.

[23] N. Sergent, P. Gelin, L. Perier-Camby, H. Praliaud, G. Thomas, Sens. Actuators B 84 (2002) 176–188.

[24] L. Urfels, P. Gelin, M. Primet, E. Tena, Preprints CAPoC6, Brussels, October 22–24, 2003, O20, pp. 203–212.