# Surface structure of bulk nickel catalysts, active in the gas-phase hydrodechlorination reaction of aromatics

Joaquim Estellé,<sup>a</sup> Javier Ruz,<sup>a</sup> Yolanda Cesteros,<sup>a</sup> Rosa Fernández,<sup>a</sup> Pilar Salagre,<sup>a</sup> Francisco Medina<sup>b</sup> and Jesús-Eduardo Sueiras<sup>b\*</sup>

<sup>a</sup> Facultat de Química, Universitat Rovira i Virgili, Pl. Imperial Tarraco, 1. 43005 Tarragona, Spain

<sup>b</sup> Escola Tècnica Superior d'Enginyeria, Universitat Rovira i Virgili, Pl. Imperial Tarraco, 1. 43005, Tarragona, Spain

Several bulk nickel catalysts obtained from different procedures have been structurally characterized using BET, XRD, SEM, TPR and TPD techniques. XRD and SEM clearly show diffentiated crystalline morphologies on the oxidized and reduced nickel phases obtained from the three catalysts studied, in agreement with the BET surface areas. TPR and TPD results show the reducibility behaviour, and that mainly atomic hydrogen chemisorbs onto the catalysts with the better crystallized and larger nickel crystallites. The catalytic activities depicted by this study for the hydrodechlorination reaction of *ortho*-dichlorobenzene show that all the bulk nickel catalysts tested yield conversions and selectivities towards benzene of >80% at temperatures >493 K. Also, the catalysts with larger octahedral crystallites showed higher TOF values and selectivities toward benzene than those with poorly crystallized structures at any reaction temperature in the range 523–393 K. The behaviour is interpreted in terms of a structure-sensitive reaction. Also, a reversible/irreversible temperature-dependent mechanism of nickel chloride formation is proposed.

It is well known that chlorinated organic compounds behave as highly toxic substances to the environment. Catalytic hydrodechlorination appears as one of the more convenient approaches to treat chlorinated organic substances with the aim of obtaining compounds with lower or null toxicities.<sup>1-6</sup>

On the other hand, the selective cleavages of the C–Cl, C–O, C–S and C–N bonds play a key role in processes related to the manufacture of fine chemicals. These reactions can be performed either over noble-metal catalysts,<sup>7-22</sup> in gas or liquid phases, or over non-noble metal catalysts under more severe experimental conditions.<sup>23-25</sup>

Also, it has been observed that supported  $Ni/\gamma-Al_2O_3$ showed catalytic activity in the gas-phase hydrodechlorination reaction of chlorinated aromatic compounds.<sup>26</sup> Interesting activity of bulk nickel catalysts has also been demonstrated in some hydrogenation reactions.<sup>27,28</sup> The mechanism of C-Cl hydrogenolysis, the self-poisoning effect by the HCl produced in the reaction, and the structure sensitivity of the latter are interesting points to be considered. These aspects have been partially studied over palladium and rhodium,<sup>7-12,18-22,29-31</sup> although research is lacking concerning nickel catalysts. Our goal consists of studying the behaviour of bulk nickel catalysts for the hydrodechlorination reaction.

We present here the results obtained from the structural characterization and the catalytic properties of three bulk nickel catalysts which have been prepared from different procedures, for the *ortho*-dichlorobenzene hydrodechlorination reaction in the gas phase.

## Experimental

## **Catalyst preparation**

Three bulk nickel catalysts, designated as catalysts 1, 2 and 3, have been obtained from nickel carbonate hydroxide tetrahydrate without and with calcination treatment at 523 K, and nickel nitrate hexahydrate calcinated at 623 K, respectively. All these precursors were reduced with pure hydrogen at a space velocity of 2300  $h^{-1}$  and a rate of 1 K min<sup>-1</sup> up to the reduction temperature of 523 K.

## Air-free sampling

The catalysts were always handled under air-free conditions after the reduction step. The catalysts were transferred in degassed isooctane and under a hydrogen atmosphere at room temperature. The isooctane surface-impregnated samples were further isolated from the air either with a gold film for the SEM study or with sticky tape for XRD monitoring, using a glove box for mounting. The catalytic activity measurements were carried out *in situ*, in the same reactor after reduction, where gas purges, positive gas pressures and Schlenk techniques were used when necessary.

## **BET** areas

BET areas were calculated from the nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2000 surface analyser, and a value of 0.164  $nm^2$  for the cross-section of the nitrogen molecule.

#### Temperature-programmed reduction (TPR)

Temperature-programmed reductions were carried out in a Perkin-Elmer TGA 7 microbalance equipped with a 273-1273 K programmable temperature furnace. The accuracy was  $\pm 1$ µg. Samples (40 mg) were first heated at a rate of 5 K min<sup>-1</sup> up to 523 K in a stream of He (80 cm<sup>3</sup> min<sup>-1</sup>) for moisture release. After cooling to room temperature under helium, they were heated again at a rate of 0.2 K min<sup>-1</sup> in a 5% vol H<sub>2</sub>-Ar flow (80 cm<sup>3</sup> min<sup>-1</sup>) up to the reduction temperature. The mass changes in the samples are a measure of the oxygen released by the solids as water and other decomposition products in the reduction processes.

#### X-Ray diffraction (XRD)

Powder X-ray diffraction patterns of the calcined samples were obtained with a Siemens D5000 diffractometer using nickel-filtered Cu-K $\alpha$  radiation. Samples were dusted on double-sided sticky tape and mounted on glass microscope slides. The patterns were recorded over the range  $10 \leq 2\theta/$ 

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degrees  $\leq 90$ , and crystalline phases were identified using the JCPDS files.

## Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained with a JEOL JSM 6400 scanning microscope operating at an accelerating voltage in the range 25-30 kV, work distance (wd) of 18-21 mm and magnification values in the range  $25\,000-45\,000 \times$ .

## **Temperature-programmed desorption (TPD)**

Temperature-programmed desorptions were obtained with a Fisons QTMD 150 gas desorption unit equipped with a mass spectrometer detector. Precursors were reduced under the same conditions described in the catalyst preparation. Then, samples were cooled at room temperature, evacuated at low pressures (<1 Pa), and heated again at a rate of 5 K min<sup>-1</sup> up to 800 K under vacuum for desorption. Hydrogen desorptions were monitored using the mass detector. The chloroaromatic chemisorptions were performed at room temperature, following hydrogen reduction and argon purge, with mixtures of benzene-, chlorobenzene- and orthodichlorobenzene-argon at molar ratios of 1:300. The temperature-programmed desorptions of the chloroaromatics were monitored following the same temperature protocol as for  $H_2$ .

## Catalytic activity determination

In a typical experiment, the catalyst (0.5 g) was placed in a fixed-bed flow reactor for hydrodechlorination of orthodichlorobenzene at 1 atm pressure, and temperatures in the range 393-523 K, with a molar ratio chloroaromatic-H<sub>2</sub> of 1:379, and a space velocity of 3000  $h^{-1}$ . Catalysts did not show diffusion restrictions. Reaction products were analysed by means of an on-line gas chromatograph HP 5890 equipped with a packed column, a flame ionization detector and at a 393 K oven temperature.

Conversions and selectivities were defined by the following equations, conversion  $(\%) = (mol \ of \ chloroaromatic$ consumed)  $\times$  100/(mol of chloroaromatic charged). Selectivity (%) = (mol of one product of reaction)  $\times 100/(mol of chloro$ aromatic consumed). The carbon mass balance of the reaction was conserved.

## **Results and Discussion**

#### **BET** areas

The unreduced NiO has a BET area of 18 m<sup>2</sup> g<sup>-1</sup>. The precursors of catalysts 1 and 2 have BET areas of 120 and 80 m<sup>2</sup>  $g^{-1}$  respectively. Table 1 shows for all samples the steep decrease of their BET areas with reduction and also gives the ratio of the number of surface nickel atoms per total number of nickel atoms [surface Ni/(surface Ni + bulk Ni)]. Catalyst 3



Fig. 1 Mass decrease vs. temperature for the TPR of the bulk unreduced nickel samples 1, 2 and 3

shows the lowest surface area and the lowest surface nickel ratio of the three catalysts studied, undoubtedly due to the highly crystalline nature of its structure.

## Temperature-programmed reduction (TPR)

Fig. 1 plots the mass changes of samples 1, 2 and 3 (starting in the forms of nickel carbonate hydroxide tetrahydrate, calcined nickel carbonate hydroxide and nickel oxide, respectively) vs. temperature in the presence of hydrogen. It shows that samples 1 and 2 started and finished their reduction processes at lower temperatures than sample 3 (non-stoichiometric crystalline nickel oxide). This effect can be explained in terms of their different surface areas and particle sizes (Table 1). It is known<sup>32</sup> that small particle sizes favour the reduction process of nickel oxide, which actually takes place by a nucleation mechanism,  $^{33-35}$  where the self-catalytic action of the amount of incipiently reduced nickel nuclei formed, and the efficiencies of hydrogen diffusion and water release during the reduction process are also relevant.

Fig. 1 also shows a high mass loss in sample 1 due to the simultaneous decomposition and reduction processes that take place. Sample 2 also exhibits a higher mass loss than that expected from the pure stoichiometric oxide, indicating the presence of initially remaining non-decomposed carbonate and the presence of the non-stoichiometric NiO phase. The slightly higher mass loss in sample 3 compared with that expected from pure NiO shows that we are reducing its nonstoichiometric phase.

## **Powder X-ray diffraction**

Fig. 2 depicts the crystalline NiO phases detected by powder X-ray diffraction for the calcined samples 2 and 3, prepared as described in the Experimental section. The characteristic NiO line intensities corresponding to catalyst 3 are indicative of its much higher crystallinity when compared with those of sample 2. The crystallite sizes determined by the Scherrer

Table 1 Summary of kinetic results, catalyst deactivations and surface metal areas obtained from some hydrodechlorination reactions

	metal area/m <sup>2</sup> g <sup>-1</sup>	Ni <sub>s</sub> /Ni <sub>r</sub> " ( × 100)		$E_{a}/kJ \text{ mol}^{-1}$			Tutatut a sustatas
catalyst			$E_d^{b}/kJ \text{ mol}^{-1}$	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	HCI	Ni/HCl
1	11.18	1.7	120	81.2	115.5	35.5	0.125
2	14.33	2.1	118	81.0	110.6	33.5	0.166
3	1.73	0.26	160	82.1	102.5	55.1	0.016

<sup>a</sup> Ratio of the number of surface nickel atoms per total number of nickel atoms. <sup>b</sup> H<sub>2</sub> desorption energies for the higher-temperature desorption peaks.



equation gave values some 25% lower than those obtained from scanning electron microscopy. Previous X-ray diffractograms of sample 1 gave patterns exhibiting lower signals and then lower crystallinity than sample 2.

## Scanning electron microscopy

Fig. 3, 4 and 5 show the scanning electron micrographs corresponding to the reduced catalysts 1, 2 and 3, respectively. From these pictures we may clearly ascertain that increasing crystalline morphologies as well as decreasing surface areas are obtained on going from catalysts 1 to 3, in agreement with the BET and XRD results. Pictures from catalysts 2 and 3 also exhibit average octahedral crystallite sizes in the range of 2000-6000 Å.

## **Temperature-programmed desorption**

Fig. 6 plots the temperature-programmed desorption of H<sub>2</sub> for the three catalysts, and shows the presence of different peaks of H<sub>2</sub> desorption for each. These peaks are representative of H<sub>2</sub> interactions of different strengths with the different nickel active sites on the surface. Increasing desorption temperatures are observed in the order 2 < 1 < 3.



100 nm

Fig. 4 Scanning electron micrograph taken from the surface of catalyst 2 (magnification  $\times 45\,000$ )





100 nm Fig. 3 Scanning electron micrograph taken from the surface of catalyst 1 (magnification × 45 000)





Fig. 6 Temperature-programmed hydrogen desorption plots obtained for catalysts 1, 2 and 3

Previous desorption tests of benzene, chlorobenzene and ortho-dichlorobenzene have shown that all desorb at much lower temperatures than  $H_2$ . Consequently, we can note the absence of adsorption of the aromatics on the catalysts at the temperatures used for the catalytic hydrodechlorination reaction (>393 K). Then, we may conclude that the reaction rates depend more on the kind of catalytic active sites and their  $H_2$  adsorption-desorption mechanism than on the nature of the aromatics.

The key role of the  $H_2$  molecule dissociation as the ratedetermining step in hydrogenation reactions is known. This dissociation process may be affected by the type of crystallographic morphology on the surface of the catalyst<sup>36</sup> and the reaction probabilities between adsorbed and incident reaction species.<sup>37–39</sup>

It is also known that hydrogen can exist in molecular, atomic and dissolved forms on several metals.<sup>40,41</sup> In order to investigate the kind of hydrogen chemisorbed on our catalysts a kinetic analysis of our TPD data was performed using the method described by Gasser,<sup>42</sup> in which the rate of gas desorption from a solid layer may fit the Arrhenius equation in the form

$$dn/dT = (vn^a/\beta)exp(-E_d/RT)$$
(1)

where *n* is the surface coverage, *a* is the kinetic order,  $E_d$  is the energy of desorption, *v* is the frequency factor, *T* is the temperature and  $\beta$  is the heating rate. The slope of the desorption curve yields dn/dT. Hence a plot of  $\ln\{(1/n^a)(dn/dT)\}$  vs. 1/T is linear for a = 1 when the reaction is first order in surface concentration. The plot is linear for a = 2 when the reaction is second order. The slope of the line gives  $E_d$ . For a known value of  $\beta$  and the established values of *a* and  $E_d$  it is then possible to calculate the pre-exponential factor *v*.

From the application of the above kinetic analysis to our catalysts, if calculations are performed on a selected portion of the curve to avoid interferences from other overlapping curves, we find that the H<sub>2</sub> desorption peaks at temperatures < 450 K show first-order desorption kinetics, which also explains the asymmetry of the desorption curves. Such firstorder desorption kinetics are assignable to hydrogen chemisorbed in molecular forms (catalysts 1 and 2 in Fig. 6). By changing the surface structure of the bulk nickel catalyst we obtain a desorption peak at ca. 600 K, which shows clear second-order desorption kinetics and a symmetric desorption curve (catalyst 3), assignable to hydrogen chemisorbed in atomic or dissociated states. The desorption energy values calculated according to eqn. (1) for the three catalysts are listed in Table 1. Catalyst 3 shows the highest value for the desorption energy in accord with the fact that all the chemisorbed hydrogen is in a dissociated form. The calculations from the desorption peaks obtained at the mid-temperature values of ca. 500 K gave straight lines for values of a = 1.2 assignable to a proportional mixture of chemisorbed molecular and atomic hydrogen (catalysts 1 and 2).

Consequently, Fig. 6 shows that catalysts 1 and 2 exhibit several surface-active sites which mainly chemisorb molecular hydrogen and a smaller amount of atomic hydrogen, whereas catalyst 3 exhibits mainly one type of active site chemisorbing hydrogen in the atomic state.

## **Catalytic activity**

Table 2 shows the catalytic activities obtained for the hydrodechlorination reaction under the conditions referred to in the Experimental section. Generally, for the catalysts studied, the only reaction products obtained were benzene and chlorobenzene. No other reaction products such as cyclohexane were detected as with Rh and Pd catalysts.<sup>8</sup>

For all catalyst, conversions yields are > 50% at 473 K, and close to 100% at higher temperatures, and benzene is the main product obtained. Selectivities of 100% or lower toward benzene are obtained from chlorobenzene and *ortho*dichlorobenzene, respectively, chlorobenzene being the only other minor product obtained.

All samples suffer a 'self-poisoning' at lower temperatures, which is due to the interaction between the metallic phase and the HCl produced in the reaction. This poisoning process is shown to be either reversible, with reduced metal regeneration at high temperatures, or irreversible at temperatures lower than 423 K following catalyst deactivation due to the surface formation of NiCl<sub>2</sub>. The poisoning effect of chloride species can be described as an initial toxicity, t, defined, according to Maurel and Barbier,<sup>43</sup> as the number of surface metal atoms deactivated by one molecule of poison, at low coverage. In practice, t corresponds to the initial slope of the deactivation curve, where the relative activity is plotted against the total amount of HCl produced by the reaction. Fig. 7 shows the loss of conversion vs. reaction time for the three catalysts at 393 K. Table 1 presents the toxicity values (calculated at 393 K) for the three bulk nickel catalysts, and shows that catalyst 3 presents an initial toxicity about 10 times lower than catalysts 1 and 2.

Table 1 also depicts the activation energies calculated either from the poisoning or the hydrodechlorination processes, using the Arrhenius equation. Slightly lower activation energy values are obtained for chlorobenzene when compared with those from the *ortho*-dichlorobenzene hydrodechlorinations according to the decrease in the initial rate of dechlorination described elsewhere for higher polychlorobenzenes.<sup>9,26</sup>

The reaction mechanism proposed for chlorobenzene hydrodechlorination is formally similar to that described by Mars and van Krebelen<sup>44</sup> for the selective oxidation of hydro-



Fig. 7 Conversion degree (%) vs. time of reaction of the bulk nickel catalysts at 393 K

Table 2 Catalytic behaviour of the bulk nickel catalysts<sup>a</sup>

		Catalyst 1			Catalyst 2			Catalyst 3		
			% molar	selectivity		% molar	selectivity		% molar	selectivity
t/min	T/K	% conv.	C <sub>6</sub> H <sub>6</sub>	C6H2CI	% conv.	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H₅Cl	% conv.	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H₅Cl
20	523	94	100	0	69	89	11	100	98	2
80		92	87	13	86	83	17	100	99	1
120		93	85	15	85	82	18	100	99	1
600		90	81	19	80	83	17	100	100	0
20	493	91	97	3	80	90	10	95	99	1
80		79	96	4	78	88	12	96	98	2
120		77	94	6	71	83	17	94	99	1
600		75	93	7	65	82	18	95	98	2
20	473	73	89	11	32	52	48	90	98	2
80		61	87	13	36	59	41	89	99	1
120		60	86	14	35	56	44	88	99	1
600		54	83	17	30	54	46	88	98	2
20	443	51	61	39	22	55	45	71	96	4
80	1.12	44	58	42	27	48	52	69	95	5
120		42	50	50	26	45	55	65	94	6
600		36	48	52	20	44	56	60	93	7
20	393	12	58	42	14	48	52	47	90	10
80	575	15	50	50	13	44	56	46	85	15
120		10	55	45	10	39	61	35	81	19
600		0	_	—	0	_		15	78	22

<sup>a</sup> Reaction conditions: ortho-dichlorobenzene hydrodechlorination at 1 bar pressure and a space velocity of 3000 h<sup>-1</sup>.

carbons:

$$Ni-H + C_6H_5Cl \xrightarrow{k_1} Ni-Cl + C_6H_6 \qquad (I)$$

$$Ni-H + HCl \longrightarrow Ni-Cl + H_2$$
 (II)

$$Ni-Cl + H_2 \xrightarrow{\kappa_3} Ni-H + HCl$$
 (III)

Steps (I) and (II) involve the oxidative formation of nickel chloride either by chlorobenzene or by HCl, and step (III) regenerates the reduced nickel from  $H_2$ . The results then obtained from this work generally show a competition between the reduction and the poisoning mechanisms both depending on the structure of the catalyst and reaction conditions (temperature and reactant partial pressures).

Table 3 lists the turnover frequencies (TOF) for the catalysts, calculated as the number of converted molecules of halogenobenzene s<sup>-1</sup> divided by the total number of surface nickel atoms assuming a cross-sectional area of 0.065 nm<sup>2</sup> for a nickel atom. These TOF values were calculated on the conversion 'plateaux' for halogenocarbon hydrodechlorinations at temperatures between 423 and 493 K and low conversions (<20%). From these results we may extract the following information.

All catalysts show an initial decrease of conversion with time before reaching a 'plateau' after about 2 h which is maintained for times > 12 h. Also, conversions decrease with temperature at reaction temperatures lower than 523 K, the catalyst becoming passivated below 423 K. The latter seems to show that the hydrodechlorination reaction and the deactivation process take place simultaneously. Surface poisoning of the bulk nickel catalysts tested seems reversible at temperatures higher than 473 K with the equilibrium, poisoning  $\rightleftharpoons$  regeneration, more shifted to one side or the other depending on the surface structure and temperature.

It is worth noting that catalyst 3, with the lowest metallic surface area of the three catalysts tested (Table 1), exhibits the highest conversions and selectivities toward benzene at all temperatures for the hydrodechlorination of *ortho*dichlorobenzene and TOF values are about 10 times higher than those of catalysts 1 or 2. This fact is in line with the ten-fold lower toxicity obtained under HCl for catalyst 3, as well as the higher apparent activation energy  $(20 \text{ kJ mol}^{-1})$  for the surface deactivation process under HCl, when compared with the other two catalysts.

Kinetic studies carried out by Coq *et al.*<sup>8</sup> show that the rate of hydrodechlorination of chlorobenzene depends on the hydrogen partial pressure with a reaction order with respect to hydrogen close to 0.5.<sup>8</sup> In line with the latter, if we consider our TPD results (Fig. 6) from which it is concluded that catalyst 3 mainly chemisorbs atomic hydrogen, we may conclude that the particular surface structure of catalyst 3 is responsible for its higher activity, defining also a structure-sensitive reaction.

Small metal particle sizes combined with amorphous structures are believed to dissociate the hydrogen molecule less

Table 3 Calculated turnover frequencies for catalysts 1–3, for the  $C_6H_5Cl$  and  $C_6H_4Cl_2$  hydrodechlorination reactions<sup>4</sup>

		T	OF	
catalyst	$T/\mathbf{K}$	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	
1	493	4433	1345	
1	483	3912	1265	
1	473	3167	1085	
1	458	1727	625	
1	435	1427	443	
1	423	1266	385	
2	493	3015	985	
2	483	2567	886	
2	473	1752	591	
2	458	1033	331	
2	435	326	123	
2	423	—	—	
3	493	30913	12678	
3	483	27812	9213	
3	473	24024	7567	
3	458	22646	7025	
3	435	14957	4578	
3	423	8566	2839	

<sup>a</sup> Reaction conditions: as in Table 2.

effectively.<sup>45,46</sup> Catalysts 1 and 2 result from near-amorphous or low crystallinity materials with metal particle sizes < 20 Å, while catalyst 3 exhibits particle sizes of  $\ge 2000$  Å and higher (Fig. 5).

## Conclusions

Several bulk nickel catalysts obtained from different procedures were structurally characterized using BET, XRD, SEM, TPR and TPD techniques. XRD and SEM techniques clearly show differentiated crystalline morphologies on the oxidized and reduced nickel phases obtained from the three catalysts studied, in agreement with the BET surface areas determined. TPR and TPD results show the reducibility behaviour of the catalysts as well as that mainly atomic hydrogen chemisorbs onto the better crystallized larger crystallites obtained from catalyst 3.

The catalytic activities examined in this study for the hydrodechlorination reaction of ortho-dichlorobenzene show that the bulk nickel catalysts tested yield high conversions and selectivities toward benzene at temperatures >493 K. Also, the catalyst with large octahedral crystallites shows higher TOF values and selectivities toward benzene than those with poorly crystallized structures at any reaction temperature in the range 523-393 K. This behaviour is interpreted in terms of a structure-sensitive reaction. Also, a reversible/irreversible temperature-dependent mechanism of nickel chloride formation is proposed.

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