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# Isokinetic behaviour in gas phase catalytic hydrodechlorination of chlorobenzene over supported nickel

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## Abstract

The kinetics of the hydrodechlorination (HDC) of chlorobenzene has been measured over Ni supported on a range of substrates (MgO, $SiO_2$, $Al_2O_3$, $Ta_2O_5$, MgO, activated carbon (AC) and graphite) of varying BET area (9–843 $m^2\,g^{-1}$) where the Ni loading was in the range 1.5–20.3% (w/w) with catalyst preparation by impregnation and deposition-precipitation. The results of a comprehensive TEM analysis is presented wherein it is demonstrated that the supported Ni phase is present in a range of sizes and morphologies. Compensation behaviour is established for chlorobenzene HDC over these catalysts with an associated isokinetic temperature ($T_{iso}$) at $669 \pm 2$ K. Application of the Selective Energy Transfer (SET) model also arrived at the same calculated $T_{iso}$ (669 K). The SET model is based on the premise of resonance between a vibrational mode of the catalyst and a vibrational mode of the reactant with a transferral of resonance energy from the catalyst to the reactant to generate the "activated complex" with subsequent reaction. In this reaction system, resonance results from energy transfer from the catalytic Ni–H vibration (at 940 $cm^{-1}$) to the out-of-plane C–H vibration (at 740 $cm^{-1}$) of the reactant. The consequence of lumping together experimental kinetic measurements that show slight variations is discussed and rationalized.

*Keywords:* Compensation behaviour; Isokinetic temperature; Selective Energy Transfer model; Catalytic hydrodechlorination; Chlorobenzene; Supported Ni catalysts

## 1. Introduction

In a previous paper [1], we have reported an isokinetic response for the catalytic hydrodehalogenation of a series of halogenated benzene derivatives over a common nickel/silica catalyst. An isokinetic effect arises where the Arrhenius plots ($\ln k$ *versus* $1/T$) for a series of very similar reactions intersect at a common temperature (the isokinetic temperature, $T_{iso}$). We demonstrated that the $T_{iso}$ for the hydrodehalogenation reactions could be accounted for using the Selective Energy Transfer (SET) model [2]. The basis for the SET model is the occurrence of a state of resonance between a vibrational mode of the catalyst system and a complimentary vibrational mode of the reacting molecule. We identified the critical reactant vibrational mode as an out-of-plane C–H vibration with optimum resonance energy transfer from the catalyst (Ni–H) vibrational mode at 940 $cm^{-1}$ [3]. The $T_{iso}$ predicted from the SET model (655 K) was very close to the value determined experimentally (658 K). In terms of reaction mechanism, we proposed a haloarene/catalyst interaction where the arene molecule is co-planar with the surface and the slow step is an activation of the out-of-plane vibrations of the C–H bond(s).

This result raised the question: will such an agreement also hold for the hydrodehalogenation of a common reactant promoted by a family of catalysts of similar or related composition? Indeed, we can flag a number of studies [4–10] where such a combination has delivered an isokinetic response. We have accordingly, as an extension to our earlier work, taken the hydrodechlorination (HDC) of chlorobenzene as a model reaction promoted by a series of supported Ni catalysts; the raw kinetic data are provided in Table 1. A consensus is emerging from the literature that catalytic hydrodehalogenation is structure sensitive, dependent on metal particle size and electronic structure [11–16]. We consider, in this study, an array of substrates ranging from a basic MgO to conventional $Al_2O_3$ and $SiO_2$ as well as $Ta_2O_5$, a highly refractive oxide

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Table 1
Collation of the experimental chlorobenzene HDC kinetic data

| Catalyst | $10^3/T$ ($K^{-1}$) | $\ln(k_{exp}$ mol $h^{-1}$ $g^{-1})$ | $E_{exp}$ (kJ $mol^{-1}$) | $\ln A_{exp}$ |
|---|---|---|---|---|
| $Ni/SiO_2$-I | 1.686 | −3.252 | 59.1 | 8.71 |
| | 1.745 | −3.669 | | |
| | 1.808 | −4.069 | | |
| | 1.859 | −4.145 | | |
| | 1.912 | −4.876 | | |
| | 2.008 | −5.460 | | |
| | 2.114 | −6.298 | | |
| $Ni/SiO_2$-II | 1.686 | −3.111 | 54.7 | 8.11 |
| | 1.745 | −3.398 | | |
| | 1.808 | −3.712 | | |
| | 1.859 | −4.056 | | |
| | 1.912 | −4.442 | | |
| | 2.008 | −5.107 | | |
| | 2.114 | −5.894 | | |
| $Ni/SiO_2$-III | 1.686 | −2.883 | 51.3 | 7.58 |
| | 1.745 | −3.165 | | |
| | 1.808 | −3.589 | | |
| | 1.859 | −3.867 | | |
| | 1.912 | −4.175 | | |
| | 2.008 | −4.834 | | |
| | 2.114 | −5.504 | | |
| $Ni/SiO_2$-IV | 1.686 | −3.789 | 63.3 | 9.22 |
| | 1.745 | −4.023 | | |
| | 1.808 | −4.482 | | |
| | 1.859 | −4.852 | | |
| | 1.912 | −5.298 | | |
| | 2.008 | −6.078 | | |
| | 2.114 | −6.969 | | |
| $Ni/SiO_2$-V | 1.686 | −3.806 | 61.5 | 8.85 |
| | 1.745 | −4.078 | | |
| | 1.808 | −4.421 | | |
| | 1.859 | −4.785 | | |
| | 1.912 | −5.224 | | |
| | 2.008 | −5.993 | | |
| | 2.114 | −6.927 | | |
| $Ni/Al_2O_3$ | 1.686 | −3.895 | 75.5 | 11.36 |
| | 1.745 | −4.551 | | |
| | 1.808 | −5.023 | | |
| | 1.859 | −5.612 | | |
| | 1.912 | −5.983 | | |
| | 2.008 | −6.912 | | |
| | 2.114 | −7.809 | | |
| Ni/MgO | 1.686 | −3.545 | 67.1 | 10.17 |
| | 1.745 | −3.945 | | |
| | 1.808 | −4.321 | | |
| | 1.859 | −4.817 | | |
| | 1.912 | −5.184 | | |
| | 2.008 | −6.021 | | |
| | 2.114 | −6.985 | | |
| Ni/AC | 1.686 | −2.887 | 40.4 | 5.35 |
| | 1.745 | −3.066 | | |
| | 1.808 | −3.343 | | |
| | 1.859 | −3.743 | | |
| | 1.912 | −4.025 | | |
| | 2.008 | −4.396 | | |
| | 2.114 | −4.893 | | |
| Ni/graphite | 1.686 | −4.913 | 119.1 | 19.20 |
| | 1.745 | −5.768 | | |
| | 1.808 | −6.856 | | |
| | 1.859 | −7.541 | | |
| | 1.912 | −8.004 | | |
| | 2.008 | −9.546 | | |
| | 2.114 | −11.127 | | |
| $Ni/Ta_2O_5$ | 1.686 | −4.223 | 99.5 | 15.91 |
| | 1.745 | −5.184 | | |
| | 1.808 | −5.712 | | |
| | 1.859 | −6.320 | | |
| | 1.912 | −6.897 | | |
| | 2.008 | −8.021 | | |
| | 2.114 | −9.543 | | |

that exhibits many of the qualities of $TiO_2$ [17]. The use of graphite, a material known [18] to induce strong metal/support interactions and a high surface area activated carbon (AC) with little or no metal/support interaction have also been investigated.

## 2. Experimental details

### 2.1. Catalyst preparation and characterization

Two $Ni/SiO_2$ catalysts were prepared by impregnation of a Cab-O-Sil 5 M silica (surface area = 194 $m^2$ $g^{-1}$) with aqueous solutions of $Ni(NO_3)_2$ to deliver a Ni content of 4.6% (w/w) (denoted $Ni/SiO_2$-I) and 8.9% (w/w) (denoted $Ni/SiO_2$-II). Prior to reaction, the catalyst precursors were activated in a 100 $cm^3$ $min^{-1}$ stream of dry $H_2$ (99.9%) at a temperature ramp (10 K $min^{-1}$, controlled using a Eurotherm 91e temperature programmer) to a final temperature of 723 K. The temperature was maintained for 18 h where the catalyst bed temperature was independently monitored using an on-line data logging system (Pico Technology, model TC-08) and found to be constant to within ±1 K. In addition, $Ni/SiO_2$-II was calcined (10 K $min^{-1}$ in 100 $cm^3$ $min^{-1}$ stream of air) at 873 K prior to reduction and the activated form is denoted $Ni/SiO_2$-III. Two further $Ni/SiO_2$ catalysts were prepared by deposition-precipitation as described elsewhere [19] and activated as above without precalcination: 1.5% (w/w) (denoted $Ni/SiO_2$-IV) and 20.3% (w/w) (denoted $Ni/SiO_2$-V). This synthesis route involves the precipitation of a nickel(II) phase onto the silica support by basification of a nickel salt solution/silica suspension *via* the decomposition of urea. Nickel loaded $Al_2O_3$, $Ta_2O_5$, and MgO (Sigma–Aldrich) were also prepared by impregnation with aqueous $Ni(NO_3)_2$ and reduced without precalcination. Butanolic $Ni(NO_3)_2$ solutions were used to impregnate activated carbon (G-60, 100 mesh, NORIT) and graphite (synthetic 1–2 μm powder, Sigma–Aldrich) supports. Aqueous solutions were not employed as the carbon support materials are hydrophobic, leading to difficulties with surface wetting that can impact on the ultimate metal dispersion [20]. The Ni content of the catalyst precursors (75–150 μm mesh range) was measured by ICP-OES (Vista-PRO, Varian Inc.) where the analysis was reproducible to within ±2%; Ni content of each sample is given in Table 2. The activated samples were