Chloride poisoning of water–gas shift activity in nickel catalysts during steam reforming

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This Letter reports preliminary findings on the role of chloride poisoning during steam reforming of chlorocarbons over nickel catalysts. When conversions of chlorocarbon are very high and thermal pyrolysis absent, the principal effect of chloride is to decrease water–gas shift and CH_4-steam reforming activity. Product carbon dioxide/carbon monoxide ratios are then far from equilibrium and methane remains unconverted when introduced into the feed. These results are linked to previously published surface science studies.

Keywords: steam reforming; nickel catalysts; chloride poisoning; sintering; water–gas shift

1. Introduction

Nickel-containing catalysts are used for steam reforming natural gas and naphtha [1], as shown for methane in the following reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

It is usually assumed the CO formed in reaction (1) rapidly reaches equilibrium via the water–gas shift reaction (2). Sulphur is the most commonly encountered poison for these reactions [2], and in some situations low levels selectively inhibit coke formation by blocking responsible surface sites [3]. In commercial operations, high concentrations of sulphur are very deleterious, and reduced activity leads to problems, such as excessively high tube wall temperatures near the inlet zone. Strong poisoning effects have also been reported for low levels of arsenic, which can devastate steam reformer performance [4]. Chloride is a poison for many metals, including copper-based water–gas shift catalysts [5]. However, although there can be low levels of chloride in commercial steam reformer feeds [6], there is little published on the effects of chloride on nickel steam reforming catalysts.

In this Letter, we report the poisoning effect of high levels of chloride on reactions (1) and (2). These results were obtained during an investigation of the destruction of chlorinated hydrocarbons by steam reforming. The reaction, e.g. for CH_3Cl

$$CH_3Cl + H_2O \rightleftharpoons CO + 2H_2 + HCl \qquad (3)$$

is similar to reaction (1) with the exception that HCl is also produced, and presumably, CO_2 is then formed via the water–gas shift reaction (2), which should reach equilibrium, as in CH_4-steam reforming. To our surprise, the products CO, CO_2, H_2 and H_2O were always far from shift equilibrium with nickel catalysts, from which we concluded that the presence of chloride species inhibited reaction (2) while reaction (3) was unaffected. Preliminary details of this effect are given here since they provide some insight into the mechanism of CH_4-steam reforming. More detailed information on the main reactions, steam reforming of chlorinated hydrocarbons, will be given in future publications.

2. Experimental

A typical small-scale laboratory unit was used in which regulated flows of gases from high pressure cylinders were mixed with steam and vaporized chlorinated hydrocarbons before injection into a packed bed of 20–40 mesh catalyst particles. Two quartz reactors were used: one containing 0.5 g of catalyst and the other approximately 50 g. Care was taken to minimize thermal pyrolysis reactions of chlorocarbons in the reactor inlet lines prior.

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Two Perkin-Elmer Sigma 1B gas chromatographs, using helium carrier gas, were used for product analyses. Unreacted chlorocarbon was analyzed using a Supelco 80/120 Carbopack B/3% SP-1500 column and a hydrogen flame ionization detector. Other gases (N_2, CO, CH_4, and H_2) were separated on the second unit with a Supelco Carbosieve G column and measured with a thermal conductivity detector. Inert nitrogen flowed at a constant rate throughout, serving as a carrier for the steam and as a tracer to aid material balance determination. Water in the product gas was condensed, the gas then scrubbed to remove HCl, and dried prior to analysis at a precision of about 5%.

The catalyst was a commercial steam reforming catalyst, Katalco 23-4 (23 wt% $NiO/\alpha\text{-}Al_2O_3$; 1–3 mm particles; porosity, 0.73; BET surface area 2 $m^2\ g^{-1}$; bed density, 1.0 $g\ cm^{-3}$). The chlorocarbons studied were representative of those in solvents and industrial streams and included CH_3Cl, CH_2Cl_2, CH_3CCl_3, $CHClCCl_2$, and CCl_2CCl_2. Experiments were run at atmospheric pressure, 550–900°C, 10^4–10^5 GHSV, and H_2O/C ratios of 3–10.

3. Results and discussion

Typical results with the smaller reactor are shown in table 1 for a 15 h CH_3Cl-steam reforming run. Conversion of chlorocarbon decreased slightly with time, due to catalyst coking formed from parallel pyrolysis reactions that occur unless the process is operated at extremely high conversion. Dry product compositions, however, remained approximately the same but were far from shift equilibrium, as indicated by values of 0.047–0.067 for K_{se}, the ratio $[CO_2][H_2]/[CO][H_2O]$, compared to the thermodynamic equilibrium constant (1.249) under these conditions. This decrease in shift activity must have occurred very quickly, possibly in the first few minutes, since K_{se} was drastically reduced in the first measurement.

Methane steam reforming tests before the run (table 2) showed reforming conversion slightly less than thermodynamic equilibrium and the water–gas shift conversion a little higher than its equilibrium value. This could be caused by a lowering of the bed temperature by the endothermic reaction. Nevertheless, the catalyst performed as expected, with close to equilibrium concentrations. Similar CH_4-steam reforming measurements under the same conditions after the run in table 1 showed a drastic reduction in both methane reforming and shift conversion, both were far from equilibrium. This could only result from chloride poisoning since carbon formation responsible for the slight drop in CH_3Cl-steam reforming conversion could not account for such a large decrease in CH_4-steam reforming activity. Treatment of the catalyst with steam for 16 h at the same temperature regenerated both CH_4-reforming and shift activity and returned CH_3Cl-reforming to the initial value.

The poisoning effect of chloride was further demonstrated when 1% CH_3Cl was injected into the feed during CH_4-steam reforming; activity fell to 0, 16.4, and 58.8% of the original value at 600, 700 and 800°C respectively. Furthermore, when methane was added to the feed during CH_3Cl-reforming, it emerged unchanged in the product stream.

These results, repeated over a wide range of temperatures, space velocities and chlorocarbon type, indicate CH_4-reforming and shift activities are effectively poisoned in the presence of fairly large partial pressures of chlorides (principally HCl), and the effect is reversible. Since activity for CH_3Cl-reforming is not reduced, it is tempting to speculate this reaction occurs on different types of sites. This will be addressed in subsequent publications, and only chloride poisoning of CH_4-reforming and water–gas shift is considered here.

A different insight into chloride effects emerged when the larger catalyst bed was used. Fig. 1 shows the results for CCl_2CCl_2-steam reforming with 64 g of catalyst at 700°C and a GHSV of $10^4\ h^{-1}$. Unlike copper catalysts, exposing nickel catalysts to chloride was not associated with extensive sintering of the metal phase: nickel crystallite sizes estimated from XRD line-broadening (Siemens D-5000) for the fresh and used catalyst were essentially the same (30 nm). This difference in behavior

Table 1
Typical results for steam reforming chlorinated hydrocarbons [a]

Time (h)	Conv. (%)	Dry product (mol%)			K_{se} [b]
		H_2	CO	CO_2	
0.50	0.99	75.3	17.9	6.8	0.0671
2.12	0.96	71.8	21.2	6.9	0.0533
3.86	0.96	71.4	21.7	6.9	0.0518
14.8	0.93	71.5	22.0	6.6	0.0470
equilibrium	1.00	75.6	3.6	20.8	1.2494 [c]

[a] Catalyst mass: 500 mg; feed: methyl chloride; temperature: 750°C; GHSV: $2 \times 10^5\ h^{-1}$; H_2O/C: 13.9.

[b] Experimental $[CO_2][H_2]/[CO][H_2O]$.

[c] Thermodynamic equilibrium constant.

Table 2
Methane steam reforming results before and after the run in table 1

Time	CH_4 conv. (%)	CO conv. (%)	K_{se} [a]
before reaction	0.96	0.66	1.629
after reaction	0.26	0.17	0.300
equilibrium	0.99	0.62	1.249 [b]

[a] Experimental $[CO_2][H_2]/[CO][H_2O]$.

[b] Thermodynamic equilibrium constant.

is in keeping with the higher melting point of nickel (1435°C) compared with copper (1063°C) and of their chlorides, $NiCl_2$ (1001°C) and CuCl (430°C). The covalent nature of the bonding in CuCl, the stable form in non-oxidizing conditions, is undoubtedly a major contributing factor to lowering its melting point. These differences result in Ni having much lower mobility than copper in the presence of chloride, even though the temperature in these experiments was some 400°C higher than normally encountered with Cu catalysts (250°C). In addition, the thermodynamics of Ni and Cu chloride formation,

$$Ni(c) + 2HCl \rightleftharpoons NiCl_2(c) + H_2 \tag{4}$$

$$Cu(c) + 2HCl \rightleftharpoons 2CuCl(c) + H_2 \tag{5}$$

are different, the free energies of reaction at 500°C being 1.77 and −22.58 kcal mol^{-1} respectively.

Water–gas shift equilibrium is known to be achieved during steam reforming of hydrocarbons over nickel catalysts [7]. However, fig. 1 shows the relative amounts of carbon dioxide and carbon monoxide in the product changed over a 15 h period. Initially the CO_2/CO ratio was 19 (equal to the value at thermodynamic equilibrium under the same conditions), but this fell to 1.07 in 15 h, with CCl_2CCl_2 conversion constant at 0.99999. This implies complete conversion of the CCl_2CCl_2 to the primary products of CO and HCl occurred quickly, most probably in the first 5% of the bed. As products passed through the remaining part of the catalyst bed two events took place. First, CO reacted with H_2O to give CO_2 and H_2, with enough catalyst present to initially bring the shift reaction to equilibrium. Second, HCl interacted with Ni to give an increasing amount of Cl-containing surface species adsorbed on the surface. With this progressive poisoning, shift activity became less and the CO_2/CO ratio dropped. Alternatively, chlorine poisoning deactivated chlorocarbon-steam reforming, and an increasing amount of bed was necessary to reach complete conversion. This left a decreasing amount of catalyst to carry out the water–gas shift conversion. In view of the results with the smaller bed given in tables 1 and 2, we prefer the first explanation, since the effect of exposure to chlorides on both CH_4-steam reforming and shift conversion is much more pronounced than the effect on chlorocarbon-steam reforming. Again, shift activity was restored to the catalyst by using chlorine-free steam.

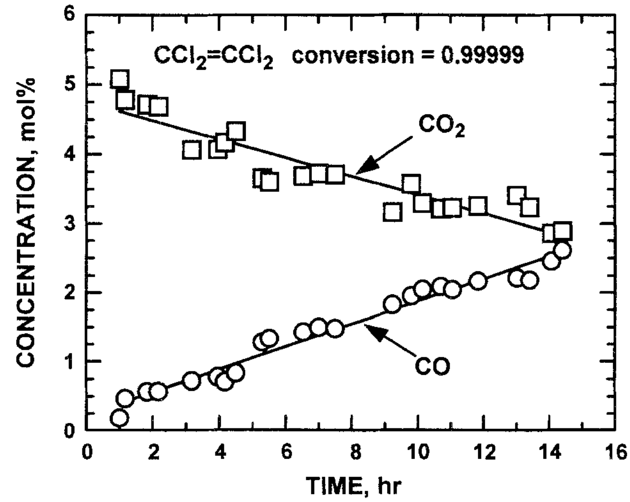

Fig. 1. Variation of CO_2/CO ratios during a typical experiment: C_2Cl_4-reforming with 64 g of catalyst at 700°C and a GHSV of 10^4 h^{-1}.

Kiskinova and Goodman, in a systematic study of preadsorbed electronegative elements on Ni(100) in well defined UHV experiments [8], found the poisoning effect on CO and H_2 adsorption increased in the sequence P, S, Cl. With Cl, these authors found the suppression of tightly bonded CO molecules increases with increasing preadsorbed overlayer coverage, dropping to zero at a coverage of 0.17. However, the Cl overlayer had no effect on methanation since Cl adatoms were quickly removed by reaction with H_2. Similarly, Erley and Wagner, using LEED on Ni(111), reported an ordered Cl superstructure with a saturation coverage close to 0.4 [9], although Cl disappeared completely from the surface above 727°C, flash desorption exhibited no QMS mass numbers from 1 to 100, ruling out atomic or molecular Cl as the desorbing species. Earlier McKinley reported nothing desorbed from a chlorine-saturated Ni surface below 527°C, but $NiCl_2$ evaporated between 527 and 877°C, both $NiCl_2$ and NiCl between 877 and 1177°C, and only NiCl above that [10]. McKinley further speculated $NiCl_2$ should be the only product when Cl coverage is high.

Steinback and Kroll found the decomposition of CH_3OH on polycrystalline Ni[111] was inhibited by Cl adsorption below about 400°C. Above this temperature, $NiCl_2$ promoted the dissociative chemisorption of CH_3OH, resulting in its decomposition by an alternative mechanism.

All of the experiments referred to used preadsorption of Cl_2 under high vacuum conditions. Under our process conditions with HCl rather than Cl_2, formation of bulk crystalline $NiCl_2$ is unfavorable above 438°C. Below this temperature, the high H_2 concentration makes the equilibrium conversion of reaction (4) low and formation of $NiCl_2$ vapor is even more unlikely. The free energy of reaction for reaction (4) with the gaseous product is almost constant at +26.5 kcal mol^{-1} from 25 to 1150°C. We therefore conclude the formation of bulk $NiCl_2$ or its evaporation from the surface is not feasible under conditions in our chlorocarbon-steam reforming experiments. Formation of surface Ni chloride species, however, cannot be excluded, and may be responsible for the observed poisoning effects.

Strong Cl chemisorption most certainly takes place, and even in the presence of H_2, an equilibrium coverage of Cl could be established. Initially, this comes from chemisorption and dissociation of the chlorocarbon in the reaction zone. Most of the adsorbed Cl is removed as HCl, but certain sites, perhaps the most energetic, remain occupied. The surface studies of Erley and Wagner [9] suggest a coverage of about 20% eliminates the ability to chemisorb CO and H_2, presumably by some type of ensemble effect, and this could explain suppression of water–gas shift activity and also, if CH_4 behaves similarly, of CH_4-steam reforming. Reforming of chlorocarbon is not so affected, either because only single Ni sites are required or chlorocarbon chemisorption occurs on sites that become available through reaction with H_2. Subsequently, if excess catalyst remains after the chlorocarbon has been completely converted, Cl poisoning occurs by chemisorption and dissociation of HCl.

We are pursuing poisoning studies of shift activity by chlorides on Ni and other metals, and a detailed report will be made at a later time.

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