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Hydrodechlorination of dichloromethane, trichloroethane, trichloroethylene and tetrachloroethylene over a sulfided Ni/Mo–γ-alumina catalyst

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Abstract

The hydrodechlorination reactions of dichloromethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene were examined over a commercial Ni/Mo–γ-alumina catalyst in a packed-bed reactor. This preliminary study was focused in the influence of the catalyst pre-treatment (sulfidation), temperature, pressure and nature of the solvent over the reaction yield. The evolution of the catalytic activity was also examined. As an overall, results indicate that catalytic hydrodechlorination might be a suitable method for the destruction of the above mentioned chlorinated compounds, since conversions to non-chlorinated organics were found to be close to 100%, operating at 100 bar and 350°C over a sulfided Ni/Mo–γ-alumina catalyst. However, the catalyst resistance to deactivation must be enhanced.

Keywords: Dichloromethane; Trichloroethane; Trichloroethylene; Tetrachloroethylene; Nickel–molybdenum/γ-alumina catalyst; Catalytic hydrodechlorination; Catalyst deactivation

1. Introduction

Dichloromethane (DCM), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE) and tetrachloroethylene (TTCE) are widely used chemicals, mainly in the degreasing of metals (DCM, TCA, TCE) and dry cleaning (TTCE). These compounds are the aliphatic organochlorine compounds which are released into the atmosphere in the greatest quantities [1], and are very harmful for the environment, as they are involved in stratospheric ozone depletion, smog formation, and global warming of the Earth [2,3]. DCM, TCE and TTCE are also carcinogenic for humans [4,5]. Consequently, DCM, TCA, TCE and TTCE are among the 17 highly dangerous chemicals included by the US Environment Protection Agency in the 33/50 Program of emissions reduction.

The conventional method for the elimination of the aforementioned compounds in a liquid organic matrix is thermal incineration. This process requires a high temperature (1000°C) as well as high energy consumption, and the presence of oxygen at high temperatures can cause the formation of highly toxic by-products such as phosgene or dioxins. Other elimination methods such as photochemical or biological degradation are limited in their applications [6,7]. Catalytic hydrogenation is an attractive alternative

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to thermal incineration for destroying organochlorine compounds as the reaction occurs at a low temperature, and organochlorine compounds are transformed into harmless non-chlorinated organic compounds that can be recovered or burned, and hydrogen chloride which can be easily separated by alkaline washing. Kalnes from UOP [8,9] demonstrated the advantage regarding energy consumption of catalytic hydrodechlorination vs. thermal incineration. Hydrogenation and hydrotreating catalysts were tested for the hydrodechlorination of organochlorine compounds. The catalytic hydrodechlorination of 1,2-dichloroethane and trichloroethylene over a rhodium on silica catalyst have been studied by Bozelli et al. [10], who reported moderate conversions (20%) and fast catalyst deactivation caused by the formation of rhodium chloride. Weiss and Krieger [11] studied the gas-phase hydrodechlorination of *cis*- and *trans*-dichloroethylenes and vinyl chloride over a Pt on η-alumina catalyst.

Nickel–molybdenum hydrotreating catalysts have been used for the hydrodechlorination of chlorobenzenes by several authors; good activity and stability being reported [12–15]. However, no data regarding the use of nickel–molybdenum hydrodesulfurization catalysts for the hydrodechlorination of aliphatic organochlorinated compounds have been published to our knowledge. There is no general agreement on the convenience of sulfidation to improve the activity of nickel–molybdenum/γ-alumina catalysts. For instance, it has been reported that a nickel–molybdenum/γ-alumina catalyst was more active for hydrodenitrogenation in a highly sulfided state, while the highest hydrodesulfurization activity was attained at moderate sulfidation levels [16], and that catalysts from Group VIII are inhibited by sulfur for hydrogenation of aromatic hydrocarbons [17]. It is generally accepted that in nickel–molybdenum catalysts, molybdenum is the active phase and nickel acts as a structural promoter, although in some recent studies the contrary is postulated [18,19]. Topsöe and Clause [20,21], on the basis of EXAFS and MES observations, reported that the γ-alumina surface is partially covered by Mo^{6+} cations in octaedral positions. Depending on the sulfidation conditions, MoS_2 slabs are formed which adopt different positions, forming phases such as Al–S–Mo and Al–Mo–O, the promoter occupying octahedral and tetrahedral positions in the cubic lattice. After typical laboratory sulfiding, nickel–molybdenum catalysts show stacks of MoS_2 ranging up to 10 layers [22].

The main objective of the present study is to test the possibility of destroying the most important aliphatic organochlorinated compounds in an organic matrix using nickel–molybdenum hydroprocessing catalysts. With this aim in mind, the effect of temperature, pressure, solvent, and catalyst pre-treatment (sulfidation) on the yield of the hydrodechlorination reaction of a mixture of DCM, TCA, TCE and TTCE, over a nickel–molybdenum/γ-alumina hydrotreating catalyst, was studied. The evolution of catalyst activity with reaction time was also studied, and catalyst samples corresponding to different reaction times were collected and characterized by nitrogen adsorption and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

The chemicals used in this work (DCM, TCA, TCE, TTCE, benzene, toluene, *n*-hexane and decane) were supplied by Panreac and Aldrich, with a minimum purity of 98%. The catalyst tested was Shell S-214, a commercial nickel–molybdenum on γ-alumina hydroprocessing catalyst, whose composition and textural characteristics are given in Table 1. The catalyst is available as pellets, which were crushed to a particle size of 0.13–0.25 mm.

2.2. Reaction studies: equipment and experimental procedure

Reactions were carried out in a high-pressure continuous packed-bed reactor. The reactor was a stainless steel cylinder with 9 mm interior diameter and 450 mm long, placed inside a tubular electric furnace equipped with five thermocouples at different reactor heights for monitoring the temperature. One gram of catalyst, mixed with 1 g alumina, was placed in the mid-section of the reactor. The bottom and top sections were packed with γ-alumina, the upper alumina-bed being used as the pre-heating zone. The height of the zone occupied by the catalyst was 71 mm, and the height of the upper and lower alumina-beds were 190 mm each. When the catalyst was used in sulfided

Table 1
Bulk composition and textural characteristics of Shell S-214 catalyst

Composition (wt%)	2.8 NiO, 13.5 MoO_3, 0.04 Na_2O, balance alumina
BET specific surface (m^2/g)	181
BJH desorption pore volume (cm^3/g)	0.52
Average pore diameter (nm)	11.1

form, it was activated in situ before use by passing 6 Nl/h of a mixture of 10% (vol.) hydrogen sulfide in hydrogen at atmospheric pressure heated to 400°C through the reactor during 4 h. The reactor was fed with a liquid that consisted of 50 ml of each of the four organochlorinated compounds dissolved in 1000 ml of a solvent, flowing downwards through the reactor, pumped by a Kontron T-414 liquid chromatography pump. Hydrogen was fed co-currently, the flow rate being controlled by a Brooks 5850 TR/X mass-flow regulator. The reaction products were collected in a stainless steel Teflon-lined cylindrical receiver. The top of the receiver was connected to a Tescom 26-1723-24 back-pressure regulator which maintained the operating pressure by venting the excess gas. Liquid samples were taken by emptying the receiver at selected time intervals. All the elements corresponding to the lines before the reactor were constructed of stainless steel, while the lines after the reactor were constructed of Hastelloy-C to protect them from the corrosion caused by the hydrogen chloride formed during the reaction. The setup, whose schematic diagram is shown in Fig. 1, was fitted with safety features such as temperature and pressure controls, and a rupture disk. An initial operational period of 4 h was allowed to permit the catalyst to reach constant activity before taking representative samples. To avoid transient effects, the samples taken after changing the operational conditions were discarded. Further details are given in [23].

2.3. Analysis and catalysts characterization

Reaction products were analyzed by gas chromatography in a Hewlett Packard 5890A apparatus equipped with an FID detector, using cycloheptane

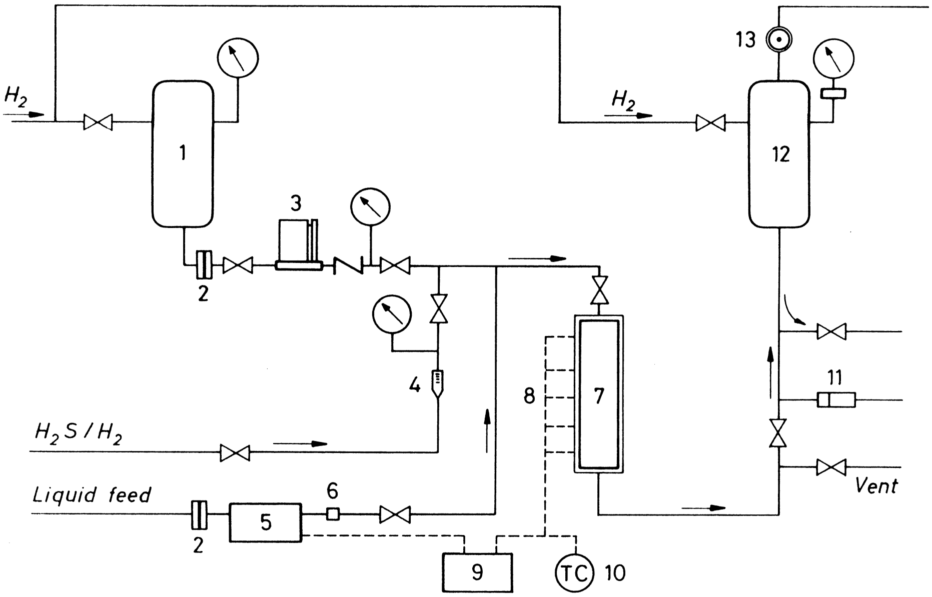

Fig. 1. Scheme of the hydrodechlorination reactor: (1) hydrogen cylinder, (2) filter, (3) mass-flow regulator, (4) rotamemeter, (5) liquid pump, (6) pulse damper, (7) reactor, (8) thermocouples, (9) recorder, (10) temperature controller, (11) rupture disk, (12) receiver, and (13) back-pressure regulator.

as internal standard and a VOCOL 60 m fused-silica capillary column. The oven was maintained at 35°C for an initial period of 15 min and then heated to 150°C at 4°C/min. Peak assignment was performed by GC-mass spectra (Hewlett Packard 5987A), and response factors were determined using standard calibration mixtures (Supelco). In all the experiments, the reaction products were hydrogen chloride, and hydrocarbons (methane and ethane), no organochlorine by-products being detected. Hydrogen chloride can be easily neutralized using a basic solution (NaOH or similar).

Textural characterization of the catalysts was performed on a Micromeritics ASAP 2000 nitrogen adsorption apparatus. Catalyst samples were observed by SEM in a JSM-6100 apparatus after Soxhlet washing with toluene during 48 h, drying at 110°C during 12 h, and gold-coating. A quantitative chemical analysis of a catalyst surface layer to a depth of about 1 μm was provided by a Link X-ray microanalyzer connected to the SEM apparatus. For the SEM-EDX analysis, catalyst samples were washed, dried, crushed, pelletized, polished and carbon-coated.

3. Results

3.1. Preliminary experiments

Preliminary experiments were carried out at 100 bar and 350°C, feeding the reactor with 0.7 ml/min (measured at room conditions) of the mixture of DCM, TCA, TCE and TTCE dissolved in *n*-hexane, and 0.8 Nl/min of hydrogen. The initial experiment was carried out with the reactor filled only with γ-alumina, with no catalyst present. Under these conditions, conversion for TCA was complete, while it was negligible for DCM, TCE and TTCE. The subsequent experiments were carried out by introducing 1.0 g of catalyst into the reactor. In an initial series of experiments, the catalyst was sulfided by the method described previously, no treatment being applied in the second series. The conversions attained, represented in Fig. 2, indicate that the catalyst is more active for the hydrodechlorination of TCE and TTCE in sulfided form. A complementary experiment was carried out with the reactor filled with low area γ-alumina, and with a feed containing only TCA; conversion for TCA in this case being 20%.

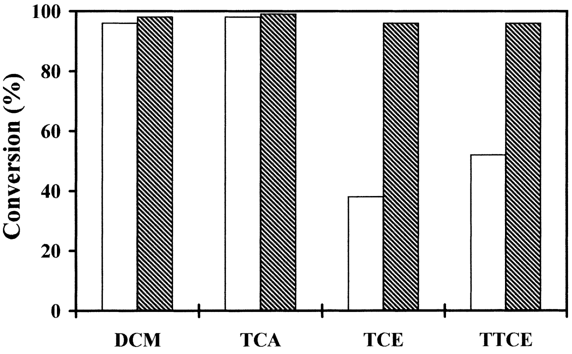

Fig. 2. Effect of catalyst sulfiding in the hydrodechlorination of DCM, TCA, TCE, and TTCE: (white area) unsulfided; (shaded area) sulfided.

3.2. Effect of temperature

The effect of temperature on the yield of the hydrodechlorination reactions was studied by operating the reactor loaded with 1 g of sulfided catalyst, with the same feeds and flow rates as in the previous paragraph, i.e. at 100 bar and temperatures of 250°C, 300°C, and 350°C. Conversions are plotted in Fig. 3. It can be observed that the reaction is complete over TCA for all the temperature range, while for DCM, TCE, and TTCE, the reaction yield increases as reaction temperature increases. The conversions attained by DCM are higher than those for TCE and TTCE.

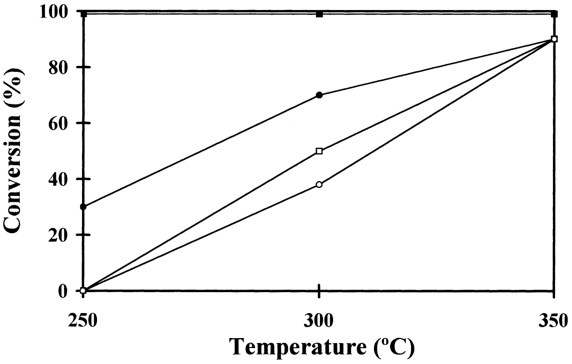

Fig. 3. Conversions of the catalytic hydrodechlorinations at 100 bar vs. reaction temperature: (●) DCM; (■) TCA; (○) TCE; (□) TTCE.

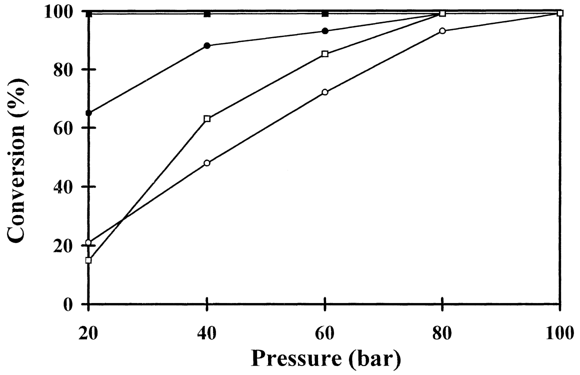

Fig. 4. Conversions of the catalytic hydrodechlorinations at 350°C vs. reaction pressure: (●) DCM; (■) TCA; (○) TCE; (□) TTCE.

3.3. *Effect of pressure*

Experiments were carried out to determine the influence of pressure on the hydrodechlorination yield with the aforementioned feeds, flow rates, and catalyst load and pretreatment, at 350°C and 20.2, 40.4, 60.6, 80.8 and 100 bar. The results, represented in Fig. 4, show that conversions increase as reaction pressure increases, with a similar trend in reactivity, TCA being completely destroyed, even for the lowest reaction pressure, and conversions for DCM being higher than those for TCE and TTCE.

3.4. *Effect of the solvent*

The effect of the solvent on the reaction yields was studied by using *n*-hexane, decane, toluene and benzene as solvents in the feed mixture, loading the reactor with 1 g catalyst, and carrying out the reaction at 100 bar and 350°C after catalyst sulfiding. It was found that the hydrodechlorination yields were unaffected by the solvent used, while the solvents themselves reacted to a slight degree: *n*-hexane and decane were cracked, forming alkanes, and benzene and toluene were partially hydrogenated, and formed small quantities of chlorobenzene. In all the cases, the solvents were hydrogenated in a proportion of 1% maximum, hydrogen remaining in the reactor in great excess.

3.5. *Catalyst deactivation*

Catalyst deactivation was studied by operating the reactor under the following conditions: 100 bar, 350°C, catalyst load 4 g (sulfided), liquid feed 0.6 ml/min of 160 ml TTCE dissolved in 1 l benzene, hydrogen feed 2 Nl/min. The evolution of TTCE conversion vs. time of run is represented in Fig. 5. The catalyst provides a very high conversion during a period of about 58 h, after which conversion decreases, reaching 45% after 104 h of run-time. At this point, the reactor was emptied, and the catalyst recovered, Soxhlet washed with toluene, and re-introduced into the reactor. After catalyst resulfiding, reactor operation was continued. The conversions attained (Fig. 5) indicate that this procedure does not lead to the catalyst regeneration.

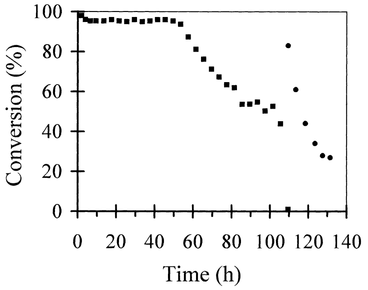

Fig. 5. Evolution of conversion with run-time for the hydrodechlorination of TTCE at 100 bar and 350°C: (■) catalyst before Soxhlet washing; (●) catalyst after Soxhlet washing.

Catalyst samples were collected after 24 h run-time (during the period of high activity) and 104 h run-time (partially deactivated). Textural characteristics of these samples, and of fresh unsulfided and fresh sulfided catalyst, are given in Table 2 and Fig. 6; a decrease in surface area, pore volume, and average pore diameter as the reaction proceeds being clearly

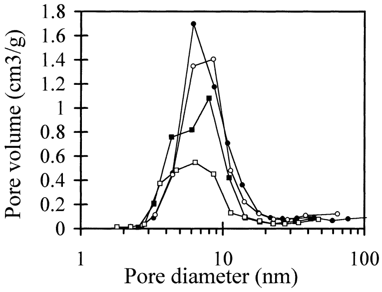

Fig. 6. Pore volume distributions for different catalyst samples: (●) fresh unsulfided; (○) fresh sulfided; (■) after 24 h; (□) after 104 h.

Table 2
Textural characteristics of different catalyst samples obtained by nitrogen adsorption

	Fresh unsulfided	Fresh sulfided	After reaction time	
			24 h	104 h
BET specific surface (m^2/g)	181	178	150	124
BJH desorption pore volume (cm^3/g)	0.52	0.46	0.36	0.25
BET average pore diameter (A)	80	75	70	63

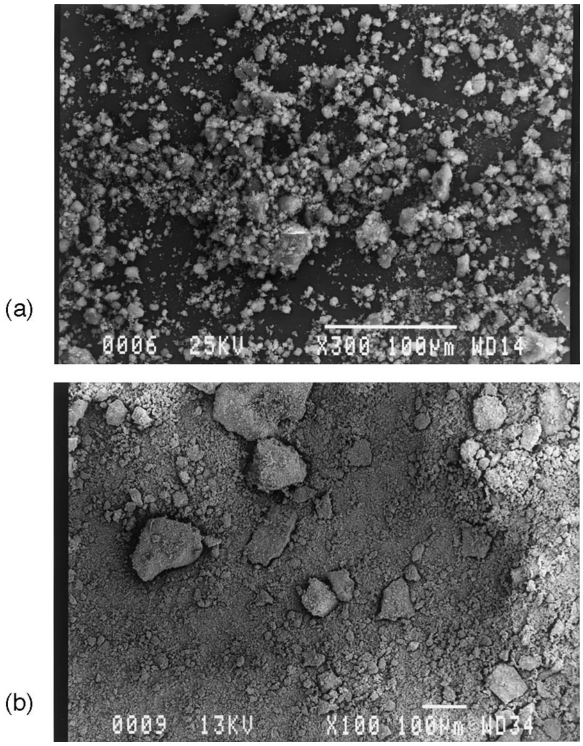

Fig. 7. SEM photographs of different catalyst samples: (a) fresh sulfided; (b) after 104 h.

observed. SEM photographs (Fig. 7) show the sintering suffered by the catalyst. EDX analysis of the catalyst surface indicates that the catalyst surface chlorine content increases from undetectable levels in the fresh sulfided catalyst to 6.5 wt% in the catalyst after 104 h reaction time.

4. Discussion

Although, the aim of this work is not to elucidate reaction mechanisms, some considerations can be made. Results of the preliminary experiments indicate that γ-alumina catalyzes the hydrodechlorination of TCA, the other compounds remaining unreacted. Several authors have shown that TCA reacts on acid alumina. Ballinger and Yates [24] observed that TCA decomposes on high surface alumina at temperatures above 400 K and atmospheric pressure, forming 1,1-dichloroethene, Al^{3+} Lewis acid sites being involved in the reaction. Similar results were obtained by Thompson et al. [25], who studied the dehydrochlorination of TCA at room temperature and atmospheric pressure on chlorine-promoted γ-alumina, finding that TCA decomposes at strong Lewis acid sites yielding 1,1-dichloroethene as the major reaction product. Archer and Simpson [26] found that chlorinated methanes and alkenes were much less reactive than TCA on Lewis acid sites. In the present work, the acidity of γ-alumina might have been enhanced by the presence of hydrogen chloride produced in the reaction, which plays an important role, in conjunction with the higher reaction temperature and pressure used, in the complete hydrodechlorination of TCA.

The different reactivity of the aliphatic (DCM, TCA) and olefinic chlorinated compounds (TCE, TTCE) can be explained by their different reaction mechanisms. The catalytic hydrodechlorination of chlorinated alkanes has been explained by some authors by means of a free-radical mechanism, the hydrogen–hydrogen bond of the hydrogen molecule, and the chlorine–carbon bond in the organochlorinated compound being activated by the catalyst [27,28]. According to this mechanism, TCA is more reactive than DCM as it has a carbon atom bonded to three chlorine atoms, while the carbon atom in DCM is bonded to two chlorine atoms. The hydrodechlorination of olefinic chlorinated compounds would take place by means of a mechanism involving the chemisorption of both hydrogen and the chlorinated compound, the addition of two hydrogen atoms to the double bond, and the elimination of hydrogen chloride.

With respect to catalyst deactivation, experimental results clearly show that this may be caused by the loss of surface area. The deposition of chlorine on the catalyst surface, detected by EDX, may also be a cause of deactivation of the catalyst, as well as possibly favoring the catalyst sintering process [29,30].

5. Conclusions

Catalytic hydrogenation on a sulfided nickel–molybdenum/γ-alumina commercial catalyst at high pressure and temperature (100 bar and 350°C) is a suitable method for the destruction of DCM, TCE and TTCE, despite the fact that catalyst resistance to deactivation should be enhanced. Under these conditions, TCA destruction is catalized by γ-alumina. The only reaction products detected are methane, ethane, and hydrogen chloride. The catalyst has been found to be more active after sulfidation. Conversions for the hydrodechlorination of DCM, TCE and TTCE increase with temperature and pressure, no influence of the solvent having been observed.

Deactivation of the catalyst was observed after 50 h of reaction. The deactivation of the catalyst may be caused by the loss of surface area and chlorine deposition.

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