JOURNAL OF CATALYSIS 74, 136–143 (1982)

Hydrodechlorination and Oligomerization of Carbon Tetrachloride over Nickel Y Zeolites

ALVIN H. WEISS AND SUSAN VALINSKI

Worcester Polytechnic Institute, Worcester, Massachusetts 01609

AND

GENADI V. ANTOSHIN

N. D. Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow B-334, USSR

Received January 10, 1981; revised November 19, 1981

A pulsed microreactor was used to study the reaction of carbon tetrachloride with hydrogen at 370°C over NiNaY, NiCuNaY, NiCrNaY, NiCoNaY, and CuNaY. Nickel was present at about 30 wt%. Activity was in the above order when catalysts were incompletely reduced at 370°C. Ni^0 in NiCoY was measured to be 40% of the total Ni by X-ray photoelectron spectroscopy. Upon complete reduction at 530°C, NiCoNaY became the most active and most selective catalyst for production of 1,1,1,2-tetrachloroethane (I). The highly specific conversion of CCl_4—0.40 mole Cl_3CCH_2Cl/mole CCl_4 at 80–100% conversion—is postulated to proceed by a free-radical mechanism initiated by H_2 dissociation on the metal $H_2 \leftrightarrows 2H\cdot$, followed by hydrodechlorination propagation reactions such as $CCl_4 + \cdot H \rightarrow \cdot CCl_3 + HCl$, $CH_2Cl_2 + \cdot H \rightarrow \cdot CH_2Cl + HCl$ and oligomerization termination reactions such as $\cdot CCl_3 + \cdot CH_2Cl \rightarrow Cl_3CCH_2Cl$. Catalyst activity and selectivity to I correlated with the order of Ni diffusion out of the supercages. Outside, on the crystallite, hydrogen from the gas stream is readily available, and hydrodechlorination is favored by excess hydrogen. Inside the supercage there should exist a relative deficiency of hydrogen, and oligomerization could be favored. That the latter process proceeds inside the supercage is evidenced by the abrupt deactivation of the catalysts after a highly active initial period. The deactivation would be related both to HCl generation and to formation of higher-molecular-weight oligomers inside the zeolite. In the absence of metal, NaY is inactive. It is probable that the Ni^0 inside and outside the supercage is not of a different nature, but the proportions in effect tailor the catalyst selectivity. Such a remarkable selectivity to Cl_3CCH_2Cl was not anticipated.

INTRODUCTION

Busch and Stöve (*1*) found in 1916 that carbon tetrachloride was reacted to completion with hydrogen at 25°C, atmospheric pressure, in aqueous or alcoholic potassium hydroxide solutions. Pd on $CaCO_3$ was used as a catalyst.

Cremer *et al.* (*2*) and then Vance and Bauman (*3*) found that complete conversion of atomic hydrogen into HCl could be had by reaction with carbon tetrachloride.

Besprozvannyi *et al.* (*4, 5*) investigated carbon tetrachloride hydrogenation in *n*-heptane solvent in the pressure range of 4 to 20 atm and a temperature range of 80 to 110°C. The catalyst used was 0.04 wt% palladium on pumice. Mechanisms involving the formation of both hydrogen and chloroform radicals were proposed to account for the formation of both $CHCl_3$ and C_2Cl_6. The authors assumed molecular hydrogen dissociation on the catalyst surface. They postulated that the $CCl_3\cdot$ radicals are transferred from the catalyst surface to the surrounding liquid medium. Subsequent radical dimerization predominates, since more hexachloroethane than chloroform was formed.

The large formation of C_2Cl_6 under liq-

0021-9517/82/030136-08$02.00/0

uid-phase conditions is an indication that oligomerization as well as hydrodechlorination occurs in the system. However, Weiss *et al.* (*6*) reported that, in the gas phase, in the range of 12 to 123°C, 50–700 Torr H_2, using 0.5% Pt on η-Al_2O_3 catalyst, no hexachloroethane was observed. The only products produced were by hydrodechlorination—$CHCl_3$ and CH_4. They also postulated a free-radical mechanism involving adsorbed molecules and radicals.

In this present work we decided to see if the selectivity of the gas-phase reaction could be deliberately controlled by using NiNaY catalysts in which diffusion of Ni^0 to the exterior of the crystallite was affected by the presence of transition metal element ions Cr^{3+}, Co^{2+}, and Cu^{2+}. We also checked the performance of CuNaY. All of the catalysts were prepared at the Zelinskii Institute of Organic Chemistry of the USSR Academy of Sciences. They have been characterized in great detail by Minachev, Antoshin, Spiro (*7*) with Yusofov (*8*) and with Savostjanov (*9*).

EXPERIMENTAL

Purified hydrogen was used as the reactant/carrier gas in the hydrodechlorination reactions and prepurified air was used to produce the hydrogen flame in the flame ionization detector. The carbon tetrachloride was reagent grade with purity greater than 99.9%.

The zeolite catalysts used in this study were

0.20 Ni NaY ($X = 5.2$),
0.28 Co NaY ($X = 3.9$),
0.28 Cr 0.34 Ni NaY ($X = 3.9$),
0.18 Cu NaY ($X = 3.4$),
0.32 Co 0.31 Ni NaY ($X = 3.9$),
0.30 Cu 0.29 Ni NaY ($X = 3.9$),

where $X = SiO_2/Al_2O_3$ ratio. Experiments were also made over NaY ($X = 5.36$) and these showed that the unexchanged NaY zeolite does not produce any appreciable conversion of the reactants involved. Since the NaY zeolite is catalytically inactive in these reactions, the Y zeolite acts only as a support for the active metal catalyst.

The pulse microreactor used in these investigations was connected to a chromatographic column inside a gas chromatograph oven. The reactor was a ¼-in. stainless-steel tube inserted in an aluminum bronze block and heated by two 150-W cartridge heaters. A thermocouple, positioned in a thermowell located in the reactor tube above the catalyst bed, was used to determine reactor temperature. The block and the reactor tube were covered on four sides by firebrick insulation. The microreactor unit was connected to the injection port of a Varian Aerograph model 1200 FID gas chromatograph.

Some of the reactions (at 370°C temperature of reduction) were carried out in a Perkin–Elmer 900 FID chromatograph. In the Perkin–Elmer system, the injection port of the gas chromatograph was used as the reactor tube. A 10-ft × ⅛-in. o.d. 10% (wt) squalane–Chromosorb W column was used for the separation of the carbon tetrachloride–hydrogen reaction products.

An experiment involved weighing and placing 1.5–2 mg of catalyst powder between two quartz wool plugs in a quartz liner. The liner was then inserted into the stainless-steel reactor tube where the catalyst was pretreated *in situ* by reduction in hydrogen at either 370 or 530°C for 2 h, 30 cm^3/min H_2, 24 psig.

After reduction of the catalyst, the reaction temperature was adjusted to 370°C and reactant was injected into the carrier gas stream.

RESULTS AND DISCUSSION

Reactions and Products

The reaction of carbon tetrachloride with hydrogen over these catalysts involves not only hydrodechlorination of carbon tetrachloride to produce chloroform, methylene chloride, methyl chloride, and methane, but also oligomerization. Dimers and higher oligomers are produced, and these oligomers also undergo hydrodechlorination. At least 12 products are formed in the reaction. Each product peak was given a peak number, and most of them were positively identified. The products are listed in Table 1.

Pulse sizes used in these studies ranged from 0.05 to 0.6 μl. A 1-μl syringe was used to measure and transfer the liquid reactant samples through a septum in the injection port into the carrier gas stream. The carrier gas, 30 cm^3/min hydrogen, is also the reactant gas. The reaction temperature was maintained at 370°C for all runs regardless of the catalyst reduction temperature. The CCl_4 reactant evaporated into the H_2 carrier gas stream was passed over the catalyst bed and the products flowed into the chromatographic column.

Hydrogen flow through the column was determined by the use of a bubble soap meter. Flow measurements were made with the reactor at 370°C and the column at room temperature.

The squalane column used in the carbon tetrachloride reaction study was maintained at 90°C for all the 370°C temperature of reduction runs except for a few runs using the Perkin–Elmer gas chromatograph. In these runs the column was programmed from 40 to 90°C at 20°C/min. All of the experiments made over the catalyst reduced at 530°C were made using the Varian Aerograph system. The commonly used peak height times width at half-height method was used to calculate peak areas in most of these experiments. The Perkin–Elmer gas chromatograph was connected to an electronic integrator which calculated the peak areas.

TABLE 1

Observed Products in $CCl_4 + H_2$ Reaction

Peak No.	Identification	Molecular Diameter (Å)
1	Methane	3.6
2	Ethane	4.4
3	Propane	5.5
4	Methyl chloride	4.5
5	Butane	5.1
6	Ethyl chloride	5.5
9	Methylene chloride	5.4
10	1,1-Dichloroethane	5.3
11	Chloroform	5.9
12	Carbon tetrachloride	6.4
13	1,1-Dichloropropane	5.2
14	1,1,1,2-Tetrachloroethane	6.7
15	Hexachloroethane	6.8

There are no peaks 7 and 8. For some of the catalysts, a peak between peaks 6 and 9 was detected and tentatively identified as 1-chloropropane. Another peak located between peaks 13 and 14, identified as 1,1,1-trichloroethane, was observed from some catalysts as a minor product. 1,2-Dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and pentachloroethane were not detected in the product. Propane, 1-chloropropane (tentatively identified), and 1,1-dichloropropane (tentative identification) were the only three-carbon compounds observed. Although butane (tentative identification) was detected, no chlorinated four-carbon hydrocarbons were observed.

Identifications were made by comparing average retention times of the peaks representing each product compound with the retention times of pure gases and chlorinated hydrocarbon liquids injected into the gas chromatograph at the carrier gas flow rate and column temperature used in the reaction gas analysis. Tentative identifications were logical guesses considering also what the peaks were identified not to be as well as boiling point, which would determine the retention time in the squalane column used.

At low conversions, the main products were chloroform, hexachloroethane, and 1,1,1,2-tetrachloroethane. At higher conversions, the main product was 1,1,1,2-tetrachloroethane.

The formation of all of the observed

TABLE 2

$CCl_4 + H_2$ Reaction Scheme for Observed Products

I. Free-radical initiation reaction

$H_2 \rightleftarrows H\cdot + \cdot H$

II. Hydrodechlorination propagation reactions

$CCl_4 + \cdot H \rightarrow \cdot CCl_3 + HCl$

$\cdot CCl_3 + H_2 \rightarrow CHCl_3 + \cdot H$

$CHCl_3 + \cdot H \rightarrow \cdot CHCl_2 + HCl$

$\cdot CHCl_2 + H_2 \rightarrow CH_2Cl_2 + \cdot H$

$CH_2Cl_2 + \cdot H \rightarrow \cdot CH_2Cl + HCl$

$\cdot CH_2Cl + H_2 \rightarrow CH_3Cl + \cdot H$

$CH_3Cl + \cdot H \rightarrow \cdot CH_3 + HCl$

$\cdot CH_3 + H_2 \rightarrow CH_4 + \cdot H$

III. Oligomerization termination reactions

$\cdot CCl_3 + \cdot CCl_3 \rightarrow Cl_3CCCl_3$

$\cdot CCl_3 + \cdot CH_2Cl \rightarrow Cl_3CCH_2Cl$

$\cdot CCl_3 + \cdot CH_3 \rightarrow Cl_3CCH_3$

$\cdot CH_2Cl + \cdot CH_2Cl \rightarrow ClH_2CCH_2Cl$

$\cdot CH_2Cl + \cdot CH_3 \rightarrow ClH_2CCH_3$

$\cdot CH_3 + \cdot CH_3 \rightarrow H_3CCH_3$

products can be described by a free-radical scheme involving initiation by hydrogen dissociation, propagation reactions that result in hydrodechlorination products, and termination reactions between adsorbed free radicals that result in oligomerization products. Table 2 shows this scheme for the observed one- and two-carbon species. The two-carbon species can undergo the hydrodechlorination reactions, of course, generating free radicals that can oligomerize and hydrodechlorinate further to the observed three- and four-carbon species.

Catalyst Activity

Figure 1 shows that at 370°C reduction temperature, the catalyst activity at 370°C declined in the order: NiNaY > NiCuNaY > NiCrNaY > NiCoNaY > CuNaY, for both high and low conversion pulses over the reduced catalyst (0.05- and 0.5-μl reactant pulse sizes used). The activity was initially high for a characteristic period for each catalyst, and then it fell rapidly. Figure 1 also shows that after the 530°C reduction, reaction at 370°C, the activity of the catalysts declined in the order: NiCoNaY > NiCuNaY > NiCrNaY > NiNaY > CuNaY.

Selectivity

Figure 2 shows selectivity charts of the major products CCl_3CH_2Cl, $CHCl_3$, and C_2Cl_6 for all of the catalysts at both 370 and 530°C reduction. Selectivity is calculated on a carbon atom basis to correct for the dimerization. CCl_4 conversion was at 370°C reaction temperature in both cases, and was varied by varying the size of the CCl_4 injection.

The specificity of the catalysts to 1,1,1,2-tetrachloroethane is remarkable. There is a change in the order of this selectivity at the two reduction temperatures:

370°C: NiNaY > CuNaY
> NiCrNaY > NiCuNaY > <u>NiCoNaY</u>,

530°C: <u>NiCoNaY</u> > NiNaY
≈ CuNaY ≈ NiCrNaY > NiCuNaY.

Table 3 shows the results of X-ray photoelectron spectroscopy of these catalysts. Perhaps incomplete reduction of Ni explains the shift of NiCoNaY from a low-activity catalyst, poorly selective to Cl_3CCH_2Cl at 370°C reduction, to a highly active and selective catalyst when reduced at 530°C. NiCrNaY and NiCuNaY do not seem to have any selectivity advantage for the oligomerization to Cl_3CCH_2Cl com-

TABLE 3

Nickel Content of Catalysts by X-Ray Photoelectron Spectroscopy

Reduction Temp.:	$Ni^0/\Sigma Ni$ (%)	
	400°C	500°C
NiNaY	90	100
NiCoNaY	>90	100
NiCrNaY	60	100
NiCuNaY	40	100

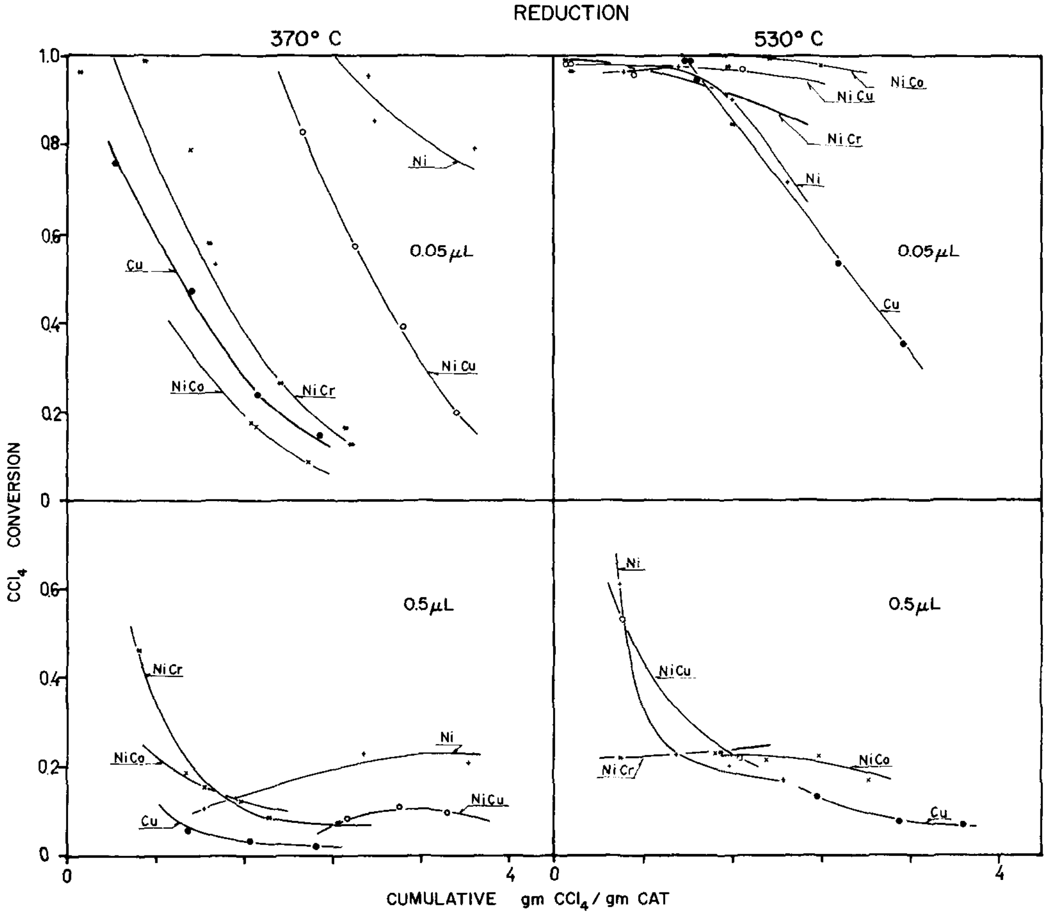

FIG. 1. Deactivation of catalysts may be a combination of oligomer accumulation in zeolite cavities and change in acidity due to HCl generation.

pared to either NiNaY or even to CuNaY. The latter catalyst does not contain nickel. It is quite selective, although of low activity.

For the nickel catalysts, the selectivity to Cl_3CCH_2Cl appears to correlate with the order of diffusion of nickel out of the supercages. This order is: NiNaY > NiCoNaY > NiCuNaY > NiCrNaY. Table 1 also lists the molecular diameters of the various products. Molecular diameters were calculated according to the method of Hirschfelder *et al.* (*10*) using viscosities estimated from critical properties (*11*). All of the products are small enough to enter into or egress from the Y supercage. Thus, the selectivity phenomena to produce oligomers might be explained on the basis that hydrodechlorination mainly occurs on nickel sites exposed to gas-phase H_2 outside the zeolite cage. Inside the cage, where there is a lower availability of H_2, there is an opportunity for condensation to occur (instead of hydrodechlorination) on the nickel sites. Such logic is also supported by the observed rapid activity decline of the catalyst after an initial period, suggesting that oligomers that are too large to egress eventually form and accumulate within the Y cage, blocking it.

If only the major product of the reaction, CCl_3CH_2Cl, is considered, a descriptive (but of course not real) reaction can be written:

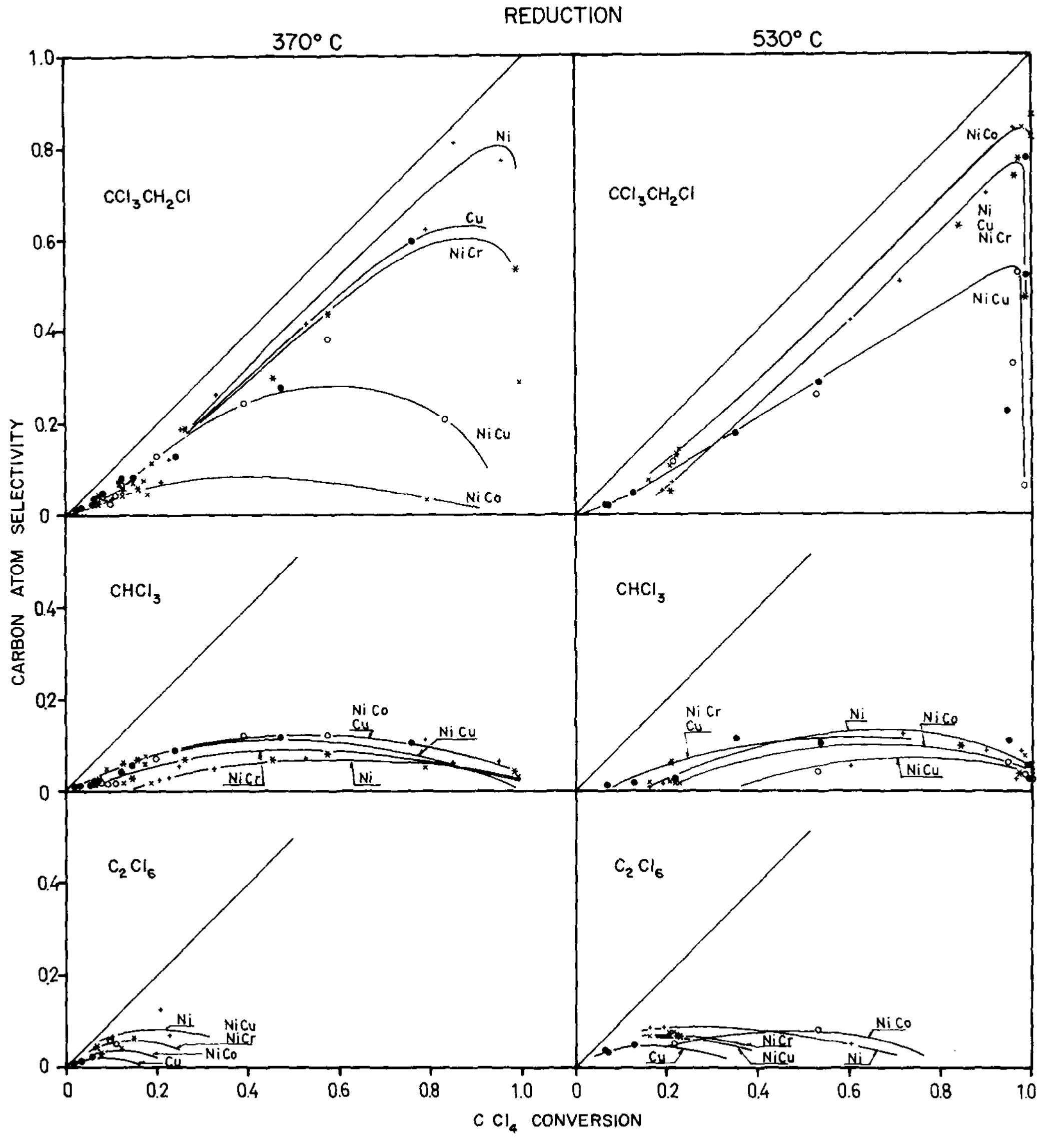

FIG. 2. At low conversions $CHCl_3$, C_2Cl_6, and CCl_3CH_2Cl are produced in equal proportions. At high conversion CCl_3CH_2Cl is the main product.

$$2CCl_4 + 3H_2 \rightarrow CCl_3CH_2Cl + 4HCl.$$

For the reaction to occur only once, four atoms of chlorine must be removed by hydrodechlorination for each time that a condensation to the ethane derivative occurs. Thus, in terms of reaction events, a highly selective catalyst is mainly a hydrochlorination catalyst—four hydrodechlorination events occur for each oligomerization event. This suggests the readily available active sites outside the zeolite cage are those that are used for hydrodechlorination and that the hydrodechlorinated radicals may then enter the cages to oligomerize.

CONCLUSIONS

When this work was initiated we had no idea whatever that it would result in such a selective process to produce 1,1,1,2-tetrachloroethane from carbon tetrachloride and hydrogen. The reaction at 370°C is capable of producing about 0.4 mole of Cl_3CCH_2Cl from each mole of CCl_4 at about 80–100% conversion, using either NiNaY reduced at 370°C or NiCoNaY reduced at 530°C. CuNaY is somewhat less selective, but nevertheless it is a low-activity effective catalyst. The degree of reduction of the copper was not checked.

In the case of the nickel-exchanged NaY catalyst, it is the nickel metal that is clearly the catalytic agent, the amount of Ni^0 being a function of reduction temperature. The X-ray photoelectron diffraction measurements established this point. However, the zeolite environment is central to the tailoring of the reaction system. Nickel that has migrated out of the supercage behaves differently than Ni^0 inside the supercage. This is controlled by the temperature of reduction and, more importantly in this work, the presence of transition metals in the impregnated NaY which affected the Ni^0 diffusion to the exterior. Selectivity in this case corresponded to the diffusion order of Ni^0:

$$\text{NiNaY} > \text{NiCoNaY} > \text{NiCuNaY} > \text{NiCrNaY}.$$

It appears that Ni^0 on the exterior of the crystallite effects hydrodechlorination, both from the diffusion order and the ready availability of hydrogen at the particle surface. Inside the zeolite, the abrupt deactivation after an active period is a reasonable suggestion of oligomer formation and accumulation in the cavity. The Y structure should not have been degraded by the HCl formed, but certainly the acidity of the environment would have been increased.

The evidence suggests that the difference in behavior of Ni^0 inside and outside is due to neither the zeolite structure per se nor to different kinds of Ni^0. Hydrodechlorination is favored on Ni^0 sites where hydrogen is present in great excess, oligomerization is favored on Ni^0 sites where there is a dearth of hydrogen. In this present system, four hydrodechlorination events are stoichiometrically required for each oligomerization event to produce Cl_3CCH_2Cl from CCl_4. Thus, the secret to tailoring the catalyst in this system is some optimal distribution of Ni inside and outside of the zeolite cage. The cage itself serves the function of providing a hydrogen partial pressure lower than that of the gas stream, permitting the oligomerization reaction that is unfavored at high hydrogen partial pressure to proceed. Studies on chemically similar nickel on amorphous silica–alumina catalysts would confirm these hypotheses if they showed that, in the absence of the zeolite cage, oligomerization is not important.

ACKNOWLEDGMENTS

Professor Kh. M. Minachev of the N. D. Zelinskii Institute of Organic Chemistry, Academy of the Sciences of the USSR, Moscow, supplied the zeolite catalysts which were used in these reaction studies. The authors are grateful to Mr. Nicolaie Naum for his help during the course of the project.

Dr. Antoshin's activity was part of the US-USSR Research Collaboration in Catalysis and was financially supported by the United States Environmental Protection Agency under EPA Contract R-802-857-01. The work was utilized by Ms. Valinsky in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering at WPI and was presented at the Seventh North American Meeting of the Catalysis Society, Boston, Massachusetts, October 11–15, 1981.

REFERENCES

1. Busch, M., and Stöve, H., *Ber.* **49,** 1063 (1916).
2. Cremer, E., Curry, J., and Polanyi, M., *Z. Phys.* **23,** 445 (1933).
3. Vance, J. E., and Bauman, W. C., *J. Chem. Phys.* **6,** 811 (1938).
4. Besprozvannyi, M. A., Kononov, N. F., and Kharhmov, V. V., *Izv. Akad. Nauk. SSSR Ser. Khim.* 1345 (1965).
5. Besprozvannyi, M. A., Kononov, N. F., and Kharhmov, V. V., *Izv. Akad. Nauk. SSSR Ser. Khim.* 1765 (1968).
6. Weiss, A. H., Gambhir, B. S., and Leon, R. B., *J. Catal.* **22,** 245 (1971).
7. Minachev, Kh. M., Antoshin, G. V., and Spiro, E. S., *Izv. Akad. Nauk. Khimiya,* 1012 (1974).

8. Minachev, Kh. M., Antoshin, G. V., Spiro, E. S., and Yusofov, Y. A., *in* "Proceedings, 6th International Congress on Catalysis, London, July 1976" (G. C. Bonds, P. B. Wells, and F. C. Tompkins, Eds.). The Chemical Society, London, 1977. See also Boreskov, G. K., and Minachev, Kh. M., "Applications of Zeolites in Catalysis," pp. 153–160. Akad. Kiadó, Budapest, 1979.
9. Minachev, Kh. M., Antoshin, G. V., Spiro, E. S., and Savostjanov, E. N., III Soviet-Japan Seminar on Catalysis, Alma Ata, USSR, 1975.
10. Hirschfelder, J. O., Curtis, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids." Wiley, New York, 1954.
11. Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids." McGraw-Hill, New York, 1977.