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Characterization of the Carbonaceous Residues on a Used Ni/SiO_2 Hydrogenation Catalyst by Temperature-Programmed Desorption Methods

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The carbonaceous residues formed during hydrogenation of 2-ethyl-2-hexenal (A) to 2-ethyl-hexanal (B) and 2-ethyl-hexanol (C) on a Ni/SiO_2 catalyst has been studied by temperature-programmed desorption (TPD), temperature-programmed hydrogenation (TPH), temperature-programmed oxidation (TPO), and by extraction. TPD displayed below 200°C dimers, B and C. Between 200 and 400°C B, C, and alkenes were detected, and at higher temperatures alkenes and some benzenes. TPH showed the same compounds, except that methane was formed above 500°C. Both TPD and TPH produced CO, CO_2, and H_2O above 450°C formed by reaction of carbonaceous deposits or H_2 with unreduced NiO. TPO showed a large peak just below 400°C, a shoulder at 400–500°C, and in some experiments a small peak at about 150°C. The H/C ratio was 1.5–2.0. Above 200°C the H/C ratio increased with temperature during TPO. The total amount of carbon atoms on the surface was 10–20 times the number of surface nickel atoms indicating that carbon was also present on the support. The extract, after extraction of the used catalyst in methanol or methylene chloride, contained mainly 2-ethyl-hexanol and some 2-ethyl-hexanal.

INTRODUCTION

Carbonaceous compounds accumulate on a catalyst during hydrogenation. This residue consists of strongly adsorbed compounds and high molecular weight compounds with low vapor pressure. It is located both on the metal and on the support.

Altham and Webb (1) studied adsorption of ^{14}C-ethylene and ^{14}C-propylene on Pt/Al_2O_3 and Pt/SiO_2. They found that a large fraction of initially adsorbed material remains on the catalyst as unreactive strongly adsorbed species. They claim that carbonaceous compounds accumulate both on the support and on the metal and that the migration of hydrogen between the metal and the support is of importance. Davis *et al.* (2) also found that adsorbed ethylene gave two kinds of surface species with different reactivity for hydrogen. The fraction with low reactivity increases with increasing adsorption temperature.

The composition of CH_x deposits depends on temperature and length of exposure. Dehydrogenation of adsorbed species may proceed below room temperature. Webb (3) found that the H/C ratio of the carbonaceous layer, formed from heptane and benzene adsorbed on Pt and heated in inert atmosphere, decreased with increased temperature reaching almost zero at 400°C. The carbon–carbon bond is stronger. Koestner *et al.* (4) observed no carbon–carbon bond scission below 150°C on Pt and Rh.

Temperature-programmed desorption (TPD) methods have been used extensively to study the composition of the accumulated compounds. However, it is often difficult to interpret the results. Some of the desorbing species are desorbing intact from the surface but others are reaction products from self-hydrogenation, decarboxylation, dehydration, cracking, etc. occurring on the catalyst surface during the TPD. For example, Komers *et al.* (5) studied the reaction of chemisorbed ethylene on Pt/SiO_2 during TPD. They found that C_2H_4 self-hydrogenated, giving a C_2H_6 peak at 356 K. At higher temperature C_2H_4 decomposed to give a CH_4 peak at 495 K. Salmerón and Somorjai (6) observed both desorption and decomposition during TPD of different unsaturated hydrocarbons on Pt(111). van Doorn *et al.* (7) used temperature-programmed oxidation (TPO) and temperature-programmed hydrogenation (TPH) to characterize the carbon and sulphur content of used catalysts. They observed both a catalytic and, at high temperature, a thermal gasification of the carbonaceous layer. In addition, Basso *et al.* (8) characterized coke on Pt/Al_2O_3 with pulsed oxidation. They observed that Pt is partially oxidized before carbon dioxide is formed. The coke on the metal is oxidized by PtO at low temperature and the coke on the support is oxidized by a migration of coke to the metal oxide or a migration of PtO to the coke.

The purpose of this work is to obtain both qualitative and quantitative information about the carbonaceous layer on a Ni/SiO_2 catalyst used in hydrogenation. The

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consecutive hydrogenation of 2-ethyl-2-hexenal to 2-ethyl-hexanal and 2-ethyl-hexanol has been selected as a model reaction. This reaction has been extensively studied at our laboratory (9–11).

EXPERIMENTAL

Catalyst

In this study silica (Girdler T1571), 5-mm pellets, ground to 0.5–1.0-mm particles, was used as the support. The silica was impregnated with a 2 *M* $Ni(NO_3)_2$ solution. The catalyst was then dried (90°C, 24 h), calcined in air (300°C, 10 h), and reduced in a hydrogen–nitrogen atmosphere (20% hydrogen, 350°C, 17 h). In order to obtain high Ni loading the impregnation, drying, calcining, and reduction procedures were repeated twice. For the second repetition, the reduction was omitted and the catalyst was kept in oxidized form. The final catalyst contained 24 wt% Ni and the metal dispersion, measured at 35°C with hydrogen adsorption (Chemisorb 2800), was 6.3%. The catalyst was reduced for 4 h at 400°C prior to the dispersion measurement. The BET surface area was 143 m^2/g.

Reaction Conditions for Hydrogenation

Before the analyses the catalyst was used for hydrogenation of 2-ethyl-2-hexenal. For the samples analyzed by TPD, TPH, and extraction, the reactor used for the hydrogenation was a plug flow glass reactor (inner diameter 15 mm) containing 1.5 g catalyst. The catalyst was reduced *in situ* at 400°C for 15 h (flow rates: 30 ml/min of He and 30 ml/min of H_2). The total flow rate during reaction was 65 ml/min and the inlet composition was 7.7% H_2, 0.3% 2-ethyl-2-hexenal, and 92% helium.

The main reactions were the consecutive reactions 2-ethyl-2-hexenal (A) → 2-ethyl-hexanal (B) → 2-ethyl-hexanol (C), but also dimerization of the aldehydes, and the formation of heptane by decarbonylization were observed. The reaction was carried out at atmospheric pressure and a reaction temperature of 120°C. The conversion of A to C was almost 100%, with only small traces of B and no A at all. Some higher hydrocarbons were also found in the outlet from the reactor. After 24 h on stream the experiment was stopped, the reactor was cooled to room temperature, and the catalyst was taken out under a nitrogen atmosphere, and divided into six samples of 0.14–0.31 g each. These were extracted with methylene chloride and methanol and analyzed by TPD and TPH.

The samples analyzed by TPO were aged in the following way: about 0.5 g catalyst was loaded in a stainless steel plug flow reactor (inner diameter 4 mm). The catalyst was reduced *in situ* for 14 h at 370°C in 5 ml/min N_2 and 5 ml/min H_2. The total flow rate during reaction was 240 ml/min and the inlet composition was 0.1% 2-ethyl-2-hexenal, 1.3% H_2, and 98.6% N_2. The conversion of A to C was close to 100%. The reaction temperature was 109°C, and after 2 days or 10 days, the reaction was stopped and the catalyst cooled in inert atmosphere. The catalyst was kept in a desiccator to prevent water adsorption before it was analyzed by TPO.

Extraction and GC/MS Analysis

The carbonaceous species were extraced from the catalyst by Soxhlet extraction with either methylene chloride or methanol. The samples were analyzed using a GC-MS system (VG TRIO-1 Benchtop GC-MS system, quadrupole mass spectrometer, 70 eV electron energy, Hewlett Packard 5890A gas chromatograph; capillary column: Nordion SE-30, 25 m, 0.32 μm, isotherm, 3.5 min 30°C, ramp 30–250°C, 7°C/min). The same GC-MS system was used for all analyses.

Temperature-Programmed Desorption, Hydrogenation, and Oxidation

The equipment for temperature-programmed analysis is described in Fig. 1. The reactor used was a quartz reactor (called the TPX reactor hereafter) of a design orginally by Cvetanovic and Amenomiya (12) described elsewhere (13). He and H_2 were passed through a Chrompack gas-clean oxygen filter and a moisture filter, and O_2 was passed through a molecular sieve. The samples analyzed were between 0.04 and 0.31 g. The reactor was heated from room temperature to 700 or 800°C at a rate of 30°C/min in the TPD and TPH experiments. The conditions used in the different experiments are described in Table 1. The outflow was analyzed by direct inlet, through a deactivated fused silica capillary from the outlet of the

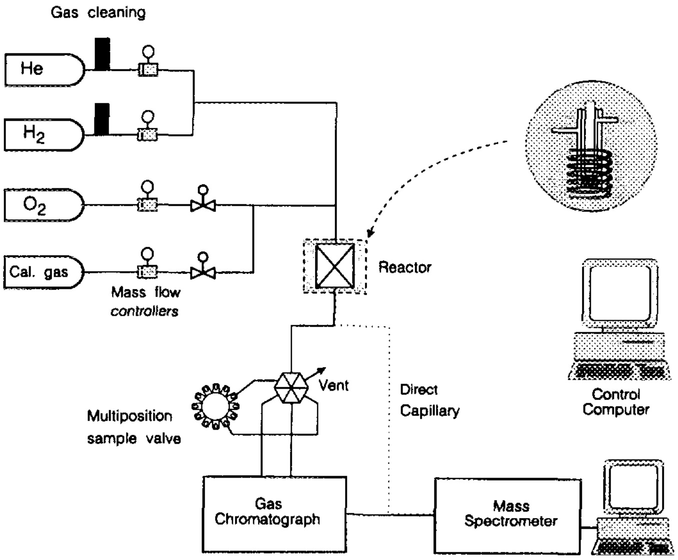

FIG. 1. Experimental setup for temperature-programmed analysis.

TABLE 1

The Conditions Used in the Different Experiments

Method	Sample weight (g)	Flow rates (ml/min)	Temperature rate (°C/min)	Final temperature (°C)
TPD	0.21	He 60	30	700
TPH	0.31	He 60 H_2 5	30	700
TPO	0.04–0.10	He 58 O_2 1.1	10	800
TPR	0.040–0.045	He 58 H_2 5	30	900

reactor into the mass spectrometer. A small part of the outlet flow went through this capillary while the major part went through a multiposition sampling valve connected to the GC-MS system. During the TPD and TPH experiments up to 11 samples were taken by the multiposition sampling valve. These samples were analyzed immediately after the TPD/TPH experiment. All tubing after the reactor, the sampling valve, and the capillary were heated to 120°C to prevent condensation of the desorbing species.

In the TPO experiments an additional reactor (the oxidation reactor) containing a 0.7-g platinum mesh was added between the TPX reactor and the capillary. This additional reactor was essential for oxidizing hydrocarbons desorbing at low temperatures. In the oxidation reactor these hydrocarbons were completely oxidized to CO_2 and H_2O at 300°C.

Calibration of the Mass Spectrometer

After the TPO experiments the mass spectrometer was calibrated with a hydrocarbon mixture containing 0.98% C_2H_2, 1.02% C_2H_4, 30.42% C_2H_6, and 67.58% N_2. Four to five different flow rates (0–0.8 ml/min) of the hydrocarbon mixture were used, while the helium and oxygen flow rates were kept constant (58.48 ml/min He, 1.07 ml/min O_2). This hydrocarbon mixture was totally oxidized to CO_2 and H_2O in the oxidation reactor. The MS signal for *m/e*44 (CO_2), *m/e*18 (H_2O), and *m/e*32 (O_2) was monitored and related to the concentration of CO_2, H_2O, and O_2. The fit between concentrations and MS signals for CO_2 and H_2O were better than that for O_2. The calibration was done the same day as the experiment.

CATALYST CHARACTERIZATION

Temperature-Programmed Desorption

Temperature-programmed desorption of the SiO_2 support showed only one peak, an H_2O peak at 150°C. No formation of H_2O from OH groups on the surface was detected up to the maximum temperature used (800°C).

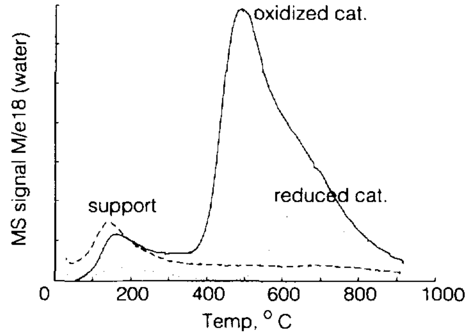

FIG. 2. Water desorbed from the support, a reduced catalyst, and an oxidized catalyst. Temperature raised by 10°C/min; flow rates: 58.5 ml/min He, 5 ml/min H_2.

TPD of the calcined catalyst also showed H_2O at 150°C and two additional small peaks, a CO_2 peak at 300°C and a NO peak at 350°C. The NO originates probably from the $Ni(NO_3)_2$ used when preparing the catalyst.

Temperature-Programmed Reduction

The catalyst was reduced in hydrogen with a temperature ramp of 30°C/min. Figure 2 shows two peaks in the water signal. The first peak at 150°C corresponds to the water peak detected during TPD and is the only peak detected during TPH of the support. The second peak results from the reduction of the NiO. The dotted curve in Fig. 2 shows the TPH curve of a catalyst reduced at 380°C for 16 h. The amount of water formed on the reduced catalyst above 350°C was about 25% of the water formed on the unreduced catalyst. If none of this water comes from the support, the degree of reduction of the reduced catalyst can be estimated to be 75%.

Temperature-Programmed Oxidation

Figure 3 shows the outlet concentration of oxygen during TPO of the reduced catalyst. The nickel metal is oxidized between 50 and 600°C. This is in the temperature

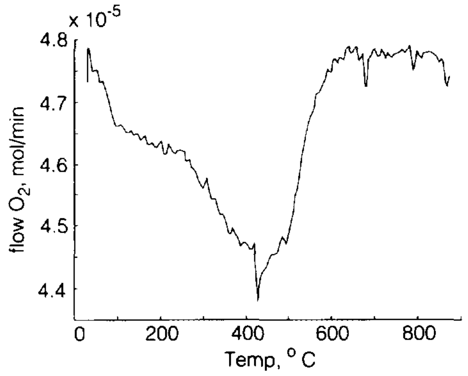

FIG. 3. Temperature-programmed oxidation of 46 mg reduced catalyst. Temperature raised by 10°C/min; flow rates: 58.5 ml/min He, 1.07 ml/min O_2.

range where oxidation of the coke on the used catalyst occurs.

RESULTS AND DISCUSSION

During the hydrogenation at 120°C, B, C, some heptane, a dimer, and some heavy hydrocarbons with unknown structures are formed. The dimer and the heavy hydrocarbons have a low vapor pressure and accumulate on the catalyst. During TPD/TPH, the dimer and the heavy hydrocarbons desorb and contaminate the equipment. In the GC-MS analyses several higher hydrocarbons are seen. Some of them are seen in all GC-MS analyses, but not in the direct inlet to the MS, and are therefore not accounted for. Since the samples were kept at ca. 100°C in the sampling loops for 1–8 h before the analysis it is probable that these compounds were formed in the sampling loops.

Because of the plug flow and the high conversion reactor operations, the catalyst particles at the beginning and end of the catalyst bed have not been exposed to the same reaction conditions. Thus the composition of the carbonaceous layer may vary, but the catalyst was mixed afterwards and the samples taken had the same composition. For the TPO analysis the catalyst was divided into two samples, one from the inlet of the reactor and one from the outlet of the reactor.

Temperature-Programmed Desorption

The TPD profile for a catalyst after 24 h on stream is shown in Fig. 4. Below 200°C mainly C, 2-ethyl-hexanoic acid, and some dimer are desorbed. These compounds are probably formed during the initial hydrogenation, and due to their low vapor pressure they condense on the support. In the interval 200–300°C A, C, and some alkene are desorbed. Very little of reactant A is desorbed. The saturated alcohol found probably originates from hydrogenation of A by hydrogen formed in the dehydrogenation of the adsorbed hydrocarbons.

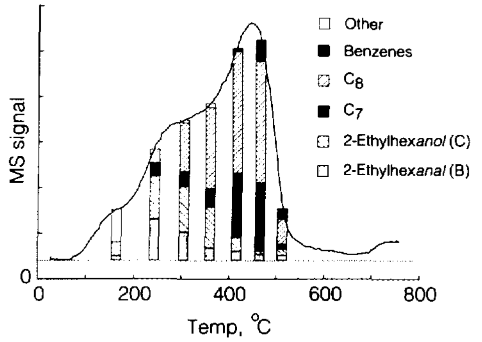

FIG. 4. Temperature-programmed desorption, total profile (except CO, CO_2, and H_2O signals), and composition of the desorbed molecules by relative areas from GC-MS analysis. Temperature raised by 30°C/min; flow rates: 60 ml/min He.

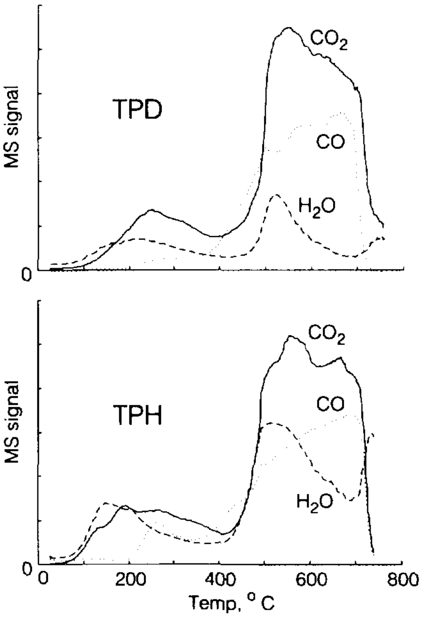

FIG. 5. Relative MS signals for CO_2 (*m/e*44*1.36), CO ((*m/e*28-*m/e*44*0.12)*1.2), and H_2O (*m/e*18*1.22) during temperature-programmed desorption and hydrogenation.

At about 250°C CO_2 starts to form together with heptene and octene, indicating that some of the heptene is formed during the TPD experiment by decomposition of the reactants. With increasing temperatures more alkene is formed. Above 350°C benzene, methyl benzene, and some heptadiene are desorbed, and above 500°C traces of methane were detected.

At 450°C there is a drastic increase in the spectra for *m/e*44 (CO_2), *m/e*28 (CO and CO_2), and *m/e*18 (H_2O) (Fig. 5), indicating that oxygen is available for reaction. The sources of this oxygen are unreduced nickel and possibly some OH groups on the silica. The catalyst was reduced for 16 h at 380°C before the reaction, which leaves about 25% of the NiO unreduced. At 700°C the spectra for *m/e*44 and *m/e*28 decrease while the spectrum for *m/e*18 increases, indicating that all reactive carbon on the catalyst is consumed.

Temperature-Programmed Hydrogenation

The MS signal from TPH (Fig. 6) is very similar to that from TPD. The main differences are that at low temperatures more saturated compounds, i.e., C and heptane, are formed and above 500°C a large amount of methane is detected.

The peak at 250°C is also higher than during TPD due to larger yields of saturated species such as heptane and octane. In TPD these products can only be formed by self-hydrogenation between the adsorbed species on the surface.

The mass spectra for *m/e*44 and *m/e*28 are similar to

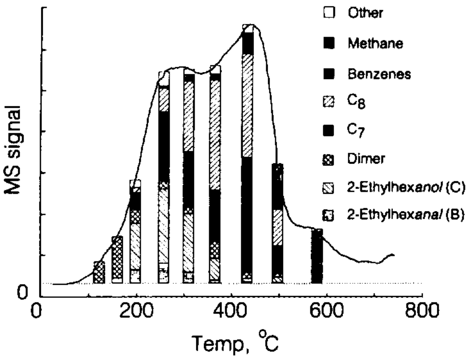

FIG. 6. Temperature-programmed hydrogenation, total profile (except CO, CO_2, and H_2O signals), and composition of the desorbed molecules by relative areas from GC-MS analysis. Temperature raised by 30°C/min; flow rates: 60 ml/min He, 5 ml/min H_2.

the TPD spectra while the mass spectrum for *m*/*e*18 is relatively higher and has a peak at 750°C (Fig. 5). This is probably due to a reduction of NiO with hydrogen and to the fact that a large amount of the coke is removed with hydrogen, leaving more oxygen available on the surface at 750°C, when only a small amount of reactive carbon is left.

Temperature-Programmed Oxidation

The CO_2 spectrum in the TPO experiment has a large peak near 350°C and a shoulder near 450°C (Fig. 7a). Without the oxidation reactor after the TPX reactor the CO_2 peak is somewhat different and hydrocarbons could be detected in the MS. This is expected since the compounds desorbing below 200°C are loosely bound and evaporate without being completely oxidized at low temperatures. Only experiments with the oxidation reactor present are accounted for when calculating the H/C ratio and the amount of carbon on the catalyst.

The H_2O curve (Fig. 7b) looks similar to the CO_2 curve but has in some experiments a peak at ca. 150°C. Our interpretation is that the peak below 200°C, corresponding to a peak in spectra for *m*/*e*18 in the TPD and TPH spectra, comes from water adsorbed on the catalyst. The broken lines in Fig. 7 come from TPO experiments where we have heated the used catalyst to 110°C for 15 min in order to desorb water.

The reactant, 2-ethyl-2-hexenal, has a H/C ratio of 1.75, and the products 2-ethyl-hexanal and 2-ethyl-hexanol, have H/C ratios of 2.0 and 2.25, respectively. The H/C ratio (Fig. 8) calculated from H_2O and CO_2 formation gives a H/C ratio of 1.48–1.57 (mean 1.53) in the interval 200–300°C, 1.58–1.80 (mean 1.68) in the interval 300–400°C, and 1.71–1.86 (mean 1.79) in the interval 400–500°C for the catalyst used on stream for 10 days. Above 550°C, the CO_2 signal is too low to calculate a H/C ratio. Water adsorbed on the catalyst causes an overestimation of the H/C ratio at low temperature. Above 200°C the H/C ratio increases with temperature during the TPO experiment. If the hydrocarbons on the support are oxidized at higher temperatures than the hydrocarbons on the metal surface, as often assumed in literature, then the hydrocarbons on the support are less dehydrogenated than the hydrocarbons on the metal surface.

Figures 8b and 8d show an experiment where the catalyst, before the TPO, was heated to 110°C for 15 min to desorb water accumulated on the catalyst. In these experiments we obtained results similar to when water had not been desorbed, except that the H/C ratio was lower below 300°C.

The H/C ratio cannot be accurately calculated from the oxygen consumption. At low oxygen consumption the calculation is very inaccurate because this consumption is calculated as the difference between two large signals. Some oxygen is also consumed in the oxidation of the nickel metal. There may also be errors in the calculation of H_2O production. Water adsorbs easily on the walls

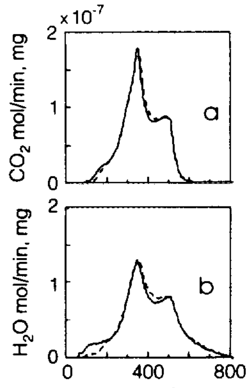

FIG. 7. CO_2 and H_2O profiles during temperature-programmed oxidation. Broken line: water desorbed before the experiment. Temperature raised with 10°C/min; flow rates: 58.5 ml/min He, 1.07 ml/min O_2.

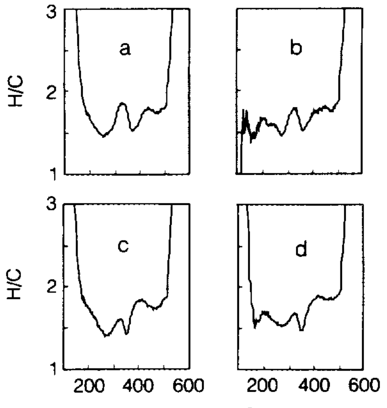

FIG. 8. HC ratio in the interval 100–600°C. (a, b) Catalyst from the inlet of the reactor and (c, d) from the outlet of the reactor; (b, d) water desorbed before the experiment.

of the reactor system and sometimes gives a high but decreasing base line, making accurate calculations difficult. By heating the reactor before each experiment and heating all tubing after the reactor we have reduced the amount of water adsorbed on the walls to negligible amounts. The water signal seems to have a small time lag relative to the CO_2 signal. This is probably due to a chromatographic effect of the support and of the reactor system walls on which water readsorbs. The peak in H/C ratio at 320°C could be due to such a time lag in the H_2O signal. The total amount of CO_2 formed gives a C/surface Ni ratio of 10–20. This corresponds to a multilayer of carbonaceous deposit on the metal; or more likely, that much of the deposit is on the support.

Extraction

Soxhlet extraction with methylene chloride and methanol was used to make a comparison between the methods of TPH/TPD and extraction. During extraction the adsorbed species on the surface are not exposed to high temperatures as in TPH or TPD and thus will not react and crack to the same extent. On the other hand the solubility of the carbonaceous residues may be limited and some species may not be soluble at all.

Extraction with either methylene chloride or methanol gave mainly 2-ethyl-hexanol but also some 2-ethyl-hexanal. In addition, 2-ethyl hexanoic acid was found in the extract but it was probably formed from oxidation of the saturated aldehyde during the extraction. There were also traces of heavier compounds, but in such small quantities that proper identification was impossible.

CONCLUSIONS

The main problem with temperature-programmed desorption methods is the difficulty to deduce, from the compounds desorbing from the catalyst surface at different temperatures, what was present on the surface during reaction. Some of these desorbing species are desorbing intact from the surface but others are reaction products from self-hydrogenation, decarboxylation, dehydration, dehydrogenation, cracking, etc. occurring on the catalyst surface during the TPD.

TPO gave a H/C ratio of 1.5–1.8 for the strongly adsorbed coke, corresponding to a somewhat dehydrogenated A. The actual composition was probably a distribution of compounds with varying H/C ratio. The carbon to surface nickel ratio is 10–20, indicating that a major part of the hydrocarbons was on the support.

The dimer and 2-ethyl-hexanol desorbing at low temperature were probably formed during the hydrogenation and physisorbed on the catalyst. Heptene and 2-ethyl-hexanal can desorb at 250°C. The fractions desorbed below 300°C were probably present from the beginning while the fractions that desorbed at higher temperaures were formed from more dehydrogenated compounds that are self-hydrogenated or in the case of heptene formed from decomposition of the aldehyde.

Below 350°C no compounds that indicated a change in the carbon skeleton desorbed. Above this temperature there was some ring closure forming benzene and methyl benzene. There was also some cracking occurring at high temperature, giving light alkenes. Both the benzenes and the light alkenes were formed during the TPD experiment, since they can, if present, desorb from a Ni surface at lower temperatures.

Multiple unsaturated compounds adsorb very strongly on the catalyst. Some heptadiene could be found at 400°C but no A was detected. Strongly dehydrogenated compounds can only desorb by self-hydrogenation or by cracking, leaving the unsaturated part on the surface.

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