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Cyclohexane, methyl- and 1,2-dimethyl-cyclohexane as the major C_{2+} products of an oxygen-free CH_4 conversion

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Abstract

Methane can be mostly converted to cyclohexane and its derivatives upon feeding a silica supported Ni and Ni–Cu catalysts with CH_4 and H_2 successively at temperatures around 275–300°C and under pressures equal to or higher than atmospheric pressure. Increasing the H_2 pressure very strongly enhances the formation of heavier products. Increasing the CH_4 pressure allows the first step of the sequence to be shortened but excessive shortening of the exposure prevents the adspecies from undergoing H_2 loss to the extent required for the formation of heavier products. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Successive feedings of certain metal catalysts with CH_4 and H_2, under appropriate conditions, has rather recently appeared as a possible way to convert CH_4 into higher hydrocarbons [1–16]. Most often, however, Pt metals have been used and CH_4 has been reacted at atmospheric pressure or, more frequently, at much lower pressures. The probable reason for having done so is that the quantity of the incoming CH_4 must not be too much higher than the monolayer capacity of the catalyst sample unless a negligible fraction of the incoming CH_4 is adsorbed (or decomposed) on the metal. Since our purpose has essentially been that of getting as broad an insight as possible into the potentialities of the surface chemistry of CH_4 on metal catalysts, we have provisionally disregarded any consideration concerning the overall yield. The interpretation of the results we have obtained with different metals has led us to anticipate positive effects from the increase of the pressure of each gas. We have been the more prompted to explore this possibility as any related industrial achievement involving natural gas would have to work at pressures well above ordinary pressure in order to be compatible with reactors of acceptable size.

Apart from platinum metals, the researchers attention has mainly been held by Co [2–4,10]. In an effort to widen the set of the metals which can exhibit interesting behaviours we have decided to examine the case of nickel with which, interestingly, copper can be alloyed in order to impede its hydrogenolysis activity [17,18].

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2. Experimental

2.1. Catalysts

Two catalysts were used in the present contribution:

1. a nickel catalyst, code-named EURONI-1, consisting of a 24.4 wt.% Ni supported on silica [19]; the average size of the Ni particles is 5 nm and the quantity of surface nickel atoms, measured through H_2 chemisorption, is ca. 8.3×10^{-4} mol of Ni/g of catalyst.
2. a nickel–copper catalyst, prepared by the group of Martin [20,21] and consisting of 16 wt.% metal supported on silica with equal molar contents of each metal; the sizes of the metallic particles range from 6 to 13 nm and their average surface composition has been shown to equal the global composition since no surface segregation has been found. The quantity of the surface metal atoms able to chemisorb H_2 is 4.2×10^{-4} mol/g of catalyst.

Each experiment was carried out using 100 mg catalyst sample. The catalyst was reduced following standard procedures in a flow of H_2 while the temperature was slowly increased up to 650°C.

2.2. Apparatus

Our experimental set-up mainly consisted of electrically actuated shut-off valves, flow-restrictors and tubing, all made of stainless steel and able to sustain pressures up to 5 MPa. The reactor was a U-shaped tube (4 mm i.d.) with a capacity of 0.4 cm^3. It was equipped with a thermocouple allowing the temperature to be measured inside the reactor chamber located between two stainless steel filters. The catalyst sample did not occupy all the reactor chamber so that, in order to prevent it from moving upon sudden changes of pressure, the unoccupied part of the volume was filled with silica powder. The reactor was located between two pressure reducers, this allowing the gas pressure to be fixed at the desired value. The flow rate was adjusted using a needle valve located on the downstream side of the second pressure reducer. Piezoelectric manometers (Jumo 4143) allowed the pressure inside the reactor to be measured.

The reactor could be fed with CH_4, H_2 or He. The gases were purified by standard procedures. In particular, the methane did not contain any hydrocarbon impurity (<0.1 ppm). Before entering the reactor, the gases were pre-heated by passing them through a stainless steel coil (length, 1 m; i.d., 2.1 mm).

2.3. Procedures

Before each experiment, the reduced catalyst was first submitted to a flow of He (50 cm^3/min, atmospheric pressure) for 20 min at 400°C in order to desorb H_2. It was then cooled at the desired temperature and exposed to a flow of CH_4 at a given flow rate for a given duration. Thereafter CH_4 was switched to H_2 (50 cm^3/min under the reactor pressure) for 10 min. In some experiments, the hydrogenation step was carried out at the temperature lower than that of the exposure to CH_4. To this end, before supplying H_2 to the catalyst, the latter was first cooled in static CH_4 at desired temperature. The interruption of the CH_4 flow stopped the removal of H_2. It also prevented adspecies from desorbing while flushing with an inert gas would have not [14].

All the C_{2+} hydrocarbons removed from the catalyst during hydrogenation were collected quantitatively in a stainless steel trap filled with glass beads, which was immersed in liquid air. The contents of the trap were chromatographically analysed as previously described [14]. The quantification of each product was achieved by measuring the corresponding peak area. The results are expressed on the basis of the carbon content of each C_{2+} hydrocarbon as this content represents the quantity of methane involved in its formation. The results of several successive experiments of each kind did not deviate from average by more than a few percent.

3. Results

We shall first examine some of the results obtained with the Ni and Ni–Cu catalysts in isothermal and dual-temperature experiments at *atmospheric pressure*. Table 1 allows us to compare the results obtained with the Ni catalyst depending on whether the hydrogenation was carried out at the same temperature as that at which the exposure to CH_4 had taken place (275°C) or the catalyst was quenched to 100°C just before hydrogenation. In the first case, C_2–C_4 alkanes

Table 1
Conversion of CH_4 over 100 mg catalyst samples in isothermal and dual-temperature cycles

Sample	Temp. (°C)	Total CH_4 converted (μmol)	Distribution (%)								
			C2	C3	C4	C5	C6	(c-C6)	C7	C8	C9
EURONI-1	275–275	4.20	25.0	40.4	25.1	7.4	2.1	(1.0)	–	–	–
EURONI-1	275–100	6.90	15.5	7.7	4.4	5.0	55.2	(54.3)	4.4	3.6	4.2
Ni–Cu	275–275	5.20	17.4	7.6	10.9	13.8	45.8	(25.1)	4.3	0.2	–
Ni–Cu	275–220	4.50	9.4	4.8	4.7	6.12	4.5	(20.6)	24.9	24.5	2.7

Step 1, exposure to CH_4: 200 cm^3/min, 5 min, 0.1 MPa.
Step 2, hydrogenation: 50 cm^3/min, 10 min, 0.1 MPa.
[a] Molar ratio of $nC_n/\sum nC_n$ $(n \geq 2)$.

were the main products and only a small amount of hexanes was formed. A significantly different product distribution resulted from the dual-temperature experiment. In this case, there was a substantial increase of the total amount of C_{2+} production. More than half of the upgraded CH_4 was converted in cyclohexane. In addition products containing up to 9 carbon atoms and corresponding to methyl-substituted cyclohexane were formed. The C_{5+} products represented 72.4% of the upgraded CH_4 instead of 9.5% in the former case and the cyclohexane was the main higher product.

The situation was very different in the case of the Ni–Cu catalyst. The C_6 species were the major heavier products even in the *isothermal* experiment; they represented almost half the upgraded methane. From that we can deduce that the hydrogenolysis reactions were slower on this Ni–Cu catalyst as compared with EURONI-1, due to the presence of Cu. However, some hydrogenolysis was also still present on this catalyst at 275°C as shown by the results of the dual-temperature experiment (275–220°C) since products containing from 7 to 9 carbon atoms were then produced in much higher amounts than in the isothermal experiment. This improvement in the distribution was obtained at the expense of the lighter products, including the C_6's but slightly less higher hydrocarbons were recovered at 220°C than at 275°C from the same adlayer.

The *influence of pressure* upon this two-step procedure, beginning with that of H_2, will now be examined, considering only the case of the Ni–Cu catalyst.

Fig. 1 represents the results of a set of experiments conducted at fixed conditions for the CH_4 chemisorption, but at different H_2 pressures. The C_{2+} productions indicated in this figure are lower than those reported above due to the lower flow rate of CH_4 and to the shorter exposures. The converted methane increased from 0.08 to 0.36 μmol when the H_2 pressure was changed from 0.1 to 0.2 MPa and the product distribution was shifted toward the heavier products (mainly cyclohexane and methyl-substituted cyclohexanes). From 0.2 to 0.4 MPa, the increase of the production was smaller (+0.14 μmol) but what remained very marked was the shift toward the heavier products. All hydrocarbons increased strongly with the H_2 pressure change from 0.1 to 0.2 MPa. With further increase up to 0.4 MPa, cyclohexane kept on increasing while the growth of methyl-cyclohexane and 1,2-dimethyl-cyclohexane was particularly strong. These experiments make clear that a given

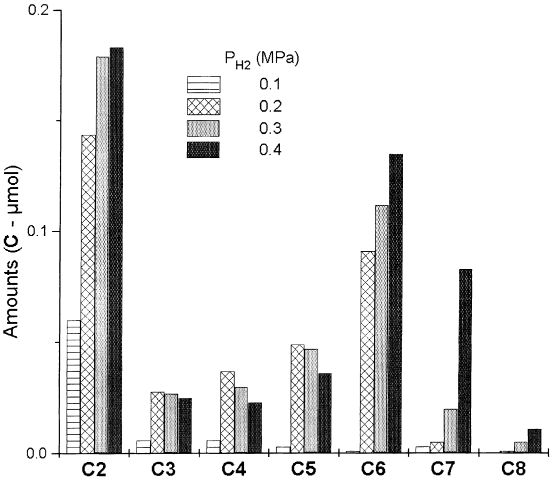

Fig. 1. Influence of the H_2 pressure on the conversion of CH_4 in the different hydrocarbons over 100 mg Ni–Cu catalyst at 275°C. Step 1, exposure to CH_4: 100 cm^3/min, 1 min, 0.1 MPa. Step 2, hydrogenation: 50 cm^3/min, 10 min, P_{H_2}.

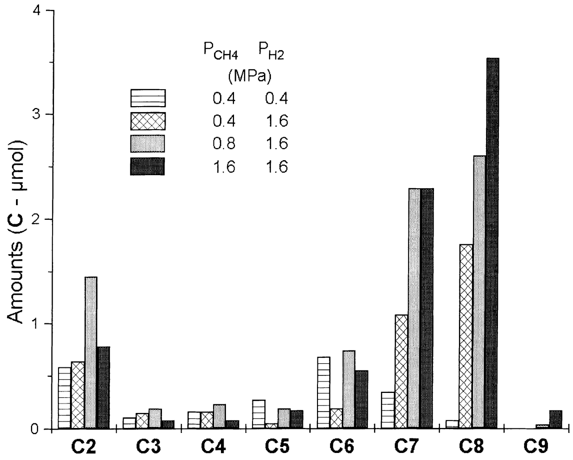

Fig. 2. Conversion of CH_4 in the different hydrocarbons over 100 mg Ni–Cu catalyst at 300°C under different pressures of CH_4 and H_2. Step 1, exposure to CH_4: 100 cm^3/min, 1 min, P_{CH_4}. Step 2, hydrogenation: 50 cm^3/min, 10 min, P_{H_2}.

exposure to CH_4 could be much better exploited when the H_2 pressure was made higher and the improvement was found in both the total C_{2+} production and the product distribution which could be strongly shifted toward the heavier products. For that reason, the H_2 pressure was always made at least equal to that of the CH_4 in the subsequent experiments.

Fig. 2 shows the results of several isothermal sequences carried out at 300°C with 1 min exposure to CH_4 under different pressures, the flow rate inside the reactor being maintained equal to 100 cm^3/min. The corresponding hydrogenation steps were carried out under 0.4 or 1.6 MPa. Their duration was 10 min, despite the fact that, for example, in the experiment carried out under a 0.4 MPa pressure of both CH_4 and H_2, about 50% of the obtained products were released within 1 min and 95% within 7 min. Subsequent retrieval of hydrocarbons such as cyclohexane, benzene, and some of their derivatives could be achieved through temperature programmed hydrogenation up to 600°C, starting after the 10 min isothermal hydrogenation. Only the products of the isothermal hydrogenation are taken into account in the results presented here. These experiments illustrate the importance of increasing the pressure of CH_4 in the first step and that of H_2 in the hydrogenation step, even if the latter has a more dramatic effect. It must be especially noted the increase of C_{7-} and C_{8-} hydrocarbons that are almost entirely methyl-cyclohexane and 1,2-dimethyl-cyclohexane.

Pressures higher than 1.6 MPa allowed us to shorten the exposures to CH_4 down to seconds but at the cost of a severe shift towards lighter products. The total C_{2+} amount was less responsive than the product distribution; for example, a 6s-exposure to 3.2 MPa of CH_4 at 325°C, followed by an hydrogenation at the same temperature and pressure, still resulted in 4.0 µmol of C_{2+} species among which were only 9% C_{5+} products.

4. Discussion

First of all, Ni appears to be able to strongly favour cyclohexane and its derivatives as major products of the two-step reaction sequence under study. This feature is obviously the result of the especially good fit of the C_6 ring to the (111) planes of this metal, as already invoked by Ceyer [22,23]. We have recently shown that the exposure of our Ni catalyst to doses of CO after preliminary exposures to CH_4 causes desorption of benzene which can therefore be reasonably considered to be the surface precursor of the cyclohexane [24]. A sufficiently high surface coverage (as a result of using an adequate temperature and duration of exposure to CH_4) and hydrogenation at temperatures sufficiently low (to reduce substantially the rate of hydrogenolysis) appear to be favourable conditions for the formation of the cyclohexane. Alloying Cu with the Ni reduces its hydrogenolysis activity and so makes it possible to obtain cyclohexane without having to cool the catalyst before hydrogenation.

We suggest that the very good fit of the benzene ring to the Ni surface can also allow adsorbed naphthalene to be formed upon increasing the surface coverage. Removal of naphthalene does not occur to any extent under our conditions but, significantly, small quantities of decalin were retrieved in some of our experiments. What is expected to be much easier is the opening of one of the naphthalene rings and the subsequent desorption of dimethyl-cyclohexane accompanied with ethane. This assumption immediately explains why only 1,2-dimethyl-cyclohexane was formed, to the exclusion of the other isomers.

There is obviously no reason for limiting the growth of adsorbed polyaromatics to the naphthalene and we can naturally see this process as the one which progressively builds up graphitic islands on the Ni surface. As we aim at retrieving the largest possible part of the adspecies as good hydrocarbons (i.e. liquid under ordinary conditions) during the second step of the process, we must avoid the excessive growth of little reactive polyaromatics during the first step.

The same considerations can help us to understand why the H_2 pressure had so much influence on the C_{2+} production as well as on the product distribution. What takes place during the hydrogenation step is not a spontaneous desorption of hydrocarbons but, instead, a forced desorption due to the fact that, in addition to giving rise to hydrogenation and hydrogenolysis processes, the hydrogen tends to displace the carbonaceous adspecies and to cover the active sites of the catalyst. For instance, regarding the release of cyclohexane and ignoring any C–C bond breaking, the hydrogenation process can be represented by:

$$\underline{S}_6C_6H_6 + 6H_2 = 6\underline{S}H + C_6H_{12}$$

where $\underline{S}$ represents an adsorption site. This would imply that the equilibrium pressure of cyclohexane, corresponding to a given coverage, is proportional to $(P_{H_2})^6$. Accordingly, the residence time of the corresponding precursor on the surface is expected to diminish rapidly if the pressure is ascribed a higher value while the other conditions are kept constant. On the contrary, the rates of the hydrogenolysis processes (to which the surface precursors are submitted at the onset of the second step) are not expected to change much with the H_2 pressure. In effect, they are proportional to the H_2 coverage and we can reasonably assume that each of the H_2 pressures used in these experiments was high enough to allow the fraction of the surface remaining unoccupied at the end of a given exposure to CH_4, to become rapidly saturated with hydrogen. Hence, any increase of the H_2 pressure strongly favours the release of any given adspecies by making its precursor escape rapidly rather than undergo the hydrogenolysis processes. The strong increases of the methyl- and dimethyl-cyclohexane, accompanied by a decrease of the cyclohexane (see Fig. 2), show that part of the cyclohexane formed at the lower pressure was due to partial hydrogenolysis of heavier precursors; these precursors could give rise to heavier products if an increased pressure of H_2 made them avoid hydrogenolysis by rapid removal from the surface.

The effect of an increase of the CH_4 *pressure* appears to be that of increasing the rate of methane adsorption and the surface coverage obtained at the end of the exposure. The decrease of cyclohexane and the parallel increase of 1,2-dimethyl-cyclohexane while methyl-cyclohexane remained constant when the pressure of CH_4 was changed from 0.8 to 1.6 MPa can be explained by the progress in the cross-linking between the adspecies due to increased surface coverage. However, shorter exposures conducted under 3.2 MPa show that, even though similar amounts of C_{2+} products can be obtained, time is necessary to the adspecies for them to undergo sufficient H_2 loss and to give rise to heavier products.

5. Conclusions

It appears from this contribution that Ni and Ni–Cu catalysts display a remarkable ability to lead the adspecies resulting from the methane chemisorption towards the formation of adsorbed benzene rings. By choosing optimum conditions for the preliminary exposure to CH_4 (temperature, pressure, flow rate, duration), one can obtain products of interest (mainly cyclohexane and its derivatives) to be released during the further hydrogenation step. Among the factors controlling this second step, the H_2 pressure exerts the most dramatic influence on the product distribution. This is because an increase of the pressure of H_2 greatly enhances its efficiency in the removal of heavier products at the expense of the hydrogenolysis of their surface precursors.

The H_2 which the methane must lose before it can be converted to higher hydrocarbons is removed, in our procedure, during the exposure step by the flow of CH_4. Very convenient at the lab-scale, this way of carrying out the reaction has allowed us to explore the chemistry of CH_4 on metal surfaces and to reveal how wealthy this chemistry can be. However, the corresponding extremely low conversions of the incoming CH_4 makes it impossible to extend this mode of H_2 removal to industrial practice. Accordingly, our effort is now being focused on the removal of H_2 in a way adapted to exposures to static methane.

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