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Nature and Reactivity of Carbonaceous Species Deposited by Ethylene on Supported Ruthenium Catalysts

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The species formed in the interaction of C_2H_4 with supported Ru catalysts have been investigated in the temperature range 296–650 K using a sequential pulse injection method. The time- and temperature-dependent reactivity of these species with hydrogen has been evaluated. The relative yields of the hydrogen-deficient dicarbon (C_2) and monocarbon (C_1) species formed at the catalyst surface depended on the temperature and the support material used, viz., molecular sieves, alumina, or glass beads. It was found that while the H_2 reacted with these species to give C_2H_6 and CH_4, in its absence, the C_2 species transformed with time to the C_1 form. Also, both the C_2 and C_1 species converted on standing to a form that was no more reactive to H_2, the rate of transformation depending on the catalyst temperature and the nature of support material. The kinetics of these transformations has been evaluated.

INTRODUCTION

Ethylene hydrogenation is one of the earliest known and most investigated catalytic reactions (*1*). It is known that over group VIII metal catalysts ethylene undergoes self-hydrogenation to yield ethane and/or methane, depending on the catalyst used, and the carbonaceous species deposited over the surface may be subsequently hydrogenated (*2–13*). The nature of the species that are formed in the interaction of C_2H_4 and the temperature- and the time-dependent modifications that they undergo are not yet well understood, especially in the case of supported metal catalysts and particularly for Ru. For instance, it is not clear whether surface species are rigidly held at one site or whether they are mobile. If mobile, then at what rate do they migrate?

In the present study, the reaction products formed in the reaction of C_2H_4 over supported Ru catalysts under an inert atmosphere and the reactivity of surface species with H_2 have been evaluated using a flow microcatalytic reactor and a method of sequential pulse injections (*14*). Three support materials with varying surface area and chemical nature have been chosen to understand the role of the support.

EXPERIMENTAL

Catalysts

Ru catalysts were prepared by soaking the support material, i.e., molecular sieve-13×, γ-alumina, or glass beads (all 60–80 mesh) in $RuCl_3 \cdot H_2O$ solution, evaporating the excess water at 375 K with constant stirring and finally reducing in H_2 for 4–5 h at 575 K. The samples thus obtained were sieved with a 60-mesh sieve to remove any fine particles.

Catalysts prepared as above were analysed for Ru content by neutron activation analysis following the decay of ^{97}Ru (216 keV $t_{1/2}$ 69.6 h) and ^{103}Ru (498 keV, $t_{1/2}$ 39.6 d) isotopes. Particulars of the three catalysts used and named as RM, RA, and RG corresponding to the support materials molecular sieves, alumina, and glass beads, respectively, are given in Table 1.

Product Analysis

A pulse flow microcatalytic reactor using He as carrier gas (34 ml min^{-1}, purified by passing through deoxo catalyst at 475 K

0021-9517/84 $3.00

TABLE 1

Description of the Catalysts

S no.	Catalyst	Nomenclature	Support material	Ru (wt%)		Surface area (m^2 g^{-1})	
				Added	Content by activation analysis	Total	Metal
1.	Ru/molecular sieve	RM	Molecular sieves-13×, Union Carbide, U.S.A.	1.6	1.56	290 ± 5	13 ± 1
2.	Ru/alumina	RA	γ-Alumina, ACC, India	0.8	0.65	135 ± 2	6 ± 1
3.	Ru/glass beads	RG	Glass beads, gas chromatography grade, F&M Scientific Corp., U.S.A.	1.5	1.25	1	—

and a molecular sieve trap at 77 K) was used in this study and has been described earlier in detail (*15*). The system consisted mainly of two pressure-actuated gas injection valves, a catalytic reactor, and a gas chromatograph, all connected in series and operated at just above atmospheric pressure. The ethylene (99.6% purity) pulse injections were made using a C_2H_4–He gas mixture (1 : 6.4) contained in a cylinder and each injected pulse was equivalent to 1.52 × 10^{-6} mol (38 μl, at NTP) of C_2H_4. One gram of catalyst sample was taken for each experiment in a stainless-steel tube reactor of 0.4-cm i.d. and the product gases were analysed using silica gel column and a thermal conductivity detector.

To evaluate the chemical reactivity of species formed over the catalyst surface, the pulses of C_2H_4 were followed by a series of H_2 pulses (each pulse ~14.5 μmol) and the effluent was analysed at each stage. The variation in the time interval between C_2H_4 and H_2 pulses gave information about the time-dependent stability of reaction intermediates formed.

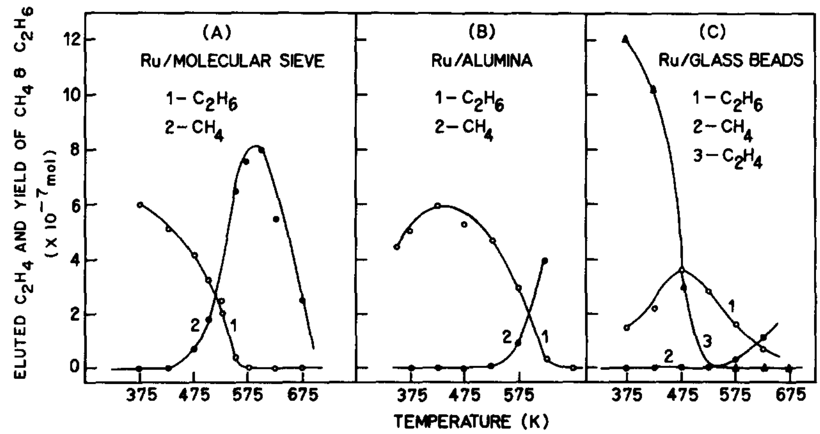


FIG. 1. Yields of CH_4 and C_2H_6 formed in the interaction of 1.52 μmol (38 μl) of C_2H_4 with catalyst surfaces in the presence of He carrier gas.

RESULTS

A. Interaction of C_2H_4

When a pulse of C_2H_4 (1.52 μmol) was injected over the catalyst in the presence of He carrier gas, the formation of C_2H_6 and CH_4 was found to occur and the yields depended on the nature of the catalyst support and the temperature. Typical yields of these products are given in Fig. 1 for different catalysts. No unreacted C_2H_4 was found to be eluted from RM and RA catalysts at any stage of the experiments. In case of RG, some unreacted C_2H_4 was eluted at temperatures below 525 K (Fig. 1c) and at temperatures above 575 K the formation of H_2 was observed, in addition to that of CH_4 and C_2H_6. In a typical experiment the yields of H_2 were 0.58, 1.18, and 1.6 μmol at temperatures of 575, 625, and 675 K, respectively. As is apparent from Fig. 1, CH_4 formation starts at 425 K in the case of RM, as compared to RA and RG where only small yields are observed even at 575 K. Also, the stage where CH_4 formation begins coincides with that where C_2H_6 formation declines (Fig. 1).

To test if the ethane formed in self-hydrogenation of ethylene undergoes a further reaction, pulses of C_2H_6 were injected over catalyst samples under He atmosphere and the products were analysed. CH_4 formation, showing a trend as in Fig. 1, was observed for all the catalysts and the typical yields of eluted C_2H_6 and that of the CH_4 formed in the case of the RM catalyst are given in Fig. 2.

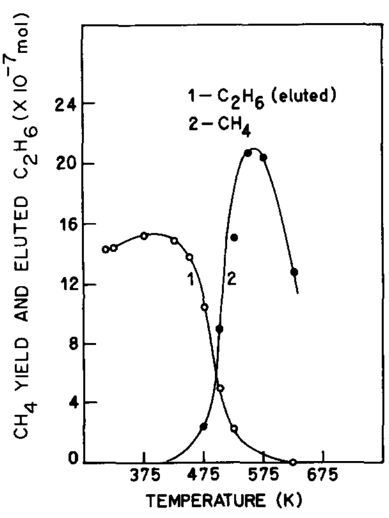


FIG. 2. Yields of CH_4 in the exposure of 1.52 μmol C_2H_6 over Ru/molecular sieve catalyst.

B. Reactivity of Surface Adsorbed Species

Following an injection of a C_2H_4 pulse and elution of reaction products as in Section A, when 10–15 successive injections of H_2 (14.5 μmol each) were made with an interval of 4 min between two injections, reaction products as given below were observed.

(i) The first H_2 injection always led to formation of C_2H_6 and/or CH_4, the yield of which depended on catalyst temperature. The relative yields of C_2H_6 and CH_4 depended also on the catalyst support used, as is evident from the data given in Fig. 3. It may be noted that the yields of CH_4 in the case of RA catalyst are about one-half of those from RM and RG in accordance with their Ru content (Table 1) while the yield of C_2H_6 decreases regularly in the order RM > RA > RG. It is also of interest to note that for all the three catalysts CH_4 yields are less at higher temperatures.

(ii) The time lapsed between C_2H_4 and the first H_2 injection had considerable influence on CH_4 and C_2H_6 yields. Figures 4 and 5 show these data for RM and RG catalysts, respectively. It may be observed that with both the catalysts at 375 K, the CH_4 yield increases with increase in the time interval between C_2H_4 and the first H_2 injection. The effect of C_2H_4–1st H_2 time gap on CH_4 yield from RA followed a behaviour similar to RM though less pronounced. At 425 K, CH_4 yields from 1st H_2 are almost independent of the time gap and at higher temperatures a continuous decrease of CH_4 yield was observed with increase in the C_2H_4–1st H_2 time gap (Figs. 4 and 5), the rate of decrease being faster at higher temperature.

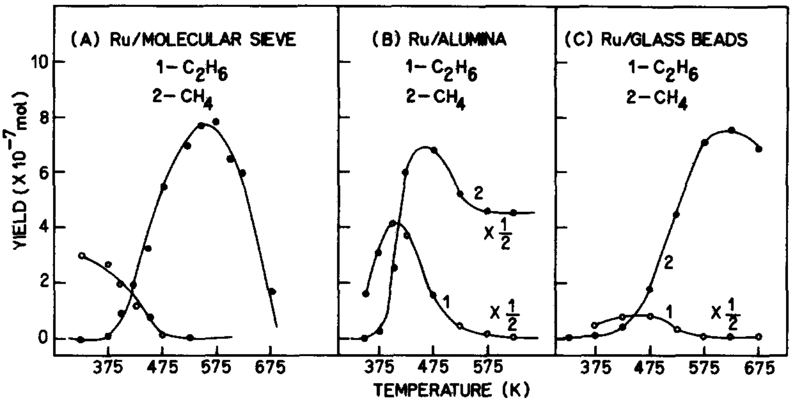


FIG. 3. CH_4 and C_2H_6 yields from the first H_2 injection subsequent to an injection of C_2H_4 over the catalyst surfaces at different temperatures in the presence of He carrier gas (C_2H_4–H_2 time interval = 5 min).

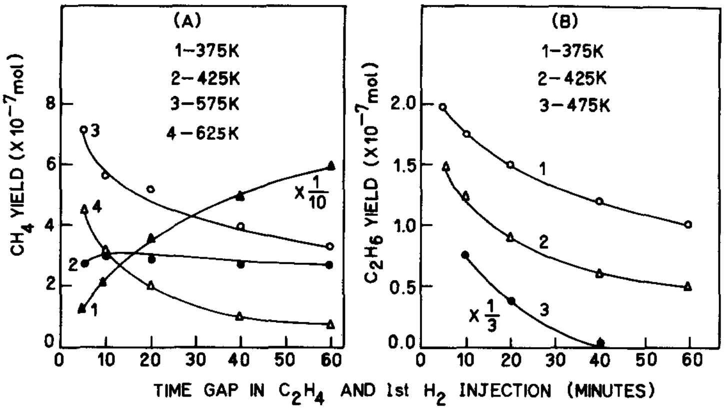


FIG. 4. CH_4 and C_2H_6 yields from the first H_2 injection made at different time intervals after an injection of 1.52 μmol of C_2H_4 over Ru/molecular sieve catalyst.

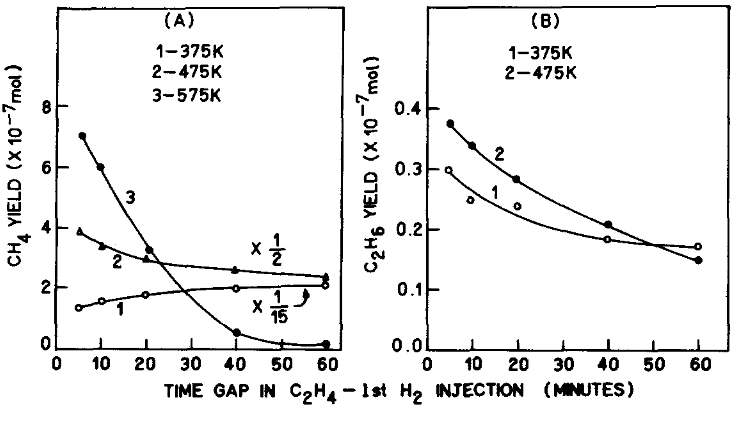


FIG. 5. CH_4 and C_2H_6 yields from the first H_2 injection made at different time intervals after an injection of 1.52 μmol of C_2H_4 over Ru/glass bead catalyst.

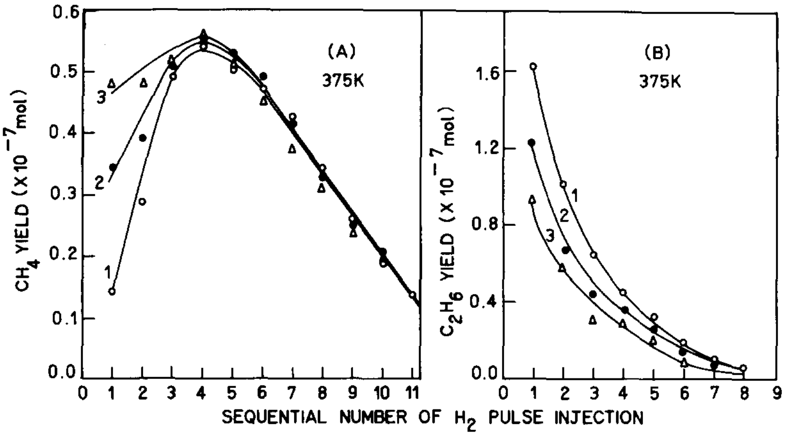


FIG. 6. CH_4 and C_2H_6 yields from the successive H_2 injections following a pulse injection of 1.52 μmol of C_2H_4 over Ru/molecular sieve catalyst at 375 K.

Curve no.:	1	2	3
C_2H_4–1st H_2 time gap (min):	5	20	40

On the other hand, the C_2H_6 yields were found to decrease with time for all C_2H_4–1st H_2 time intervals and at all catalyst temperatures studied.

(iii) After the first H_2 injection as mentioned above, when further H_2 injections were successively made with an interval of 4 min, each injection gave rise to CH_4 and/or C_2H_6 formation. The yields of these reaction products depended again on various parameters such as catalyst temperature, time gap between C_2H_4 and first H_2 injection, and catalyst support material. A typical result for RM catalyst at 375 K is shown in Fig. 6 for various C_2H_4–1st H_2 time intervals. It may be noted that the CH_4 yield increases for 4–5 H_2 pulse injections and then shows a decrease for subsequent injections. At higher temperatures, no such increase in CH_4 yield was observed, as is seen in Fig. 7 where data for different catalyst temperatures are included. Similar behavior of CH_4 and C_2H_6 yields was observed for RA and RG catalysts. It is important to note in Fig. 6 that for a particular catalyst the significant difference in CH_4 or C_2H_6 yields occurs only for the first three or four H_2 injections and for further H_2 injections the yields of CH_4 or C_2H_6 are nearly the same.

To evaluate the effect of temperature and that of support material on the recovery of the laid-down carbon subsequent to injection of a C_2H_4 pulse over the catalyst surface, the amount of total carbon recovered [evaluated by summation of the yields of C_2H_6 and/or CH_4 in the initial disproportionation reaction (Fig. 1) and on subsequent H_2 injections] are plotted in Fig. 8 for

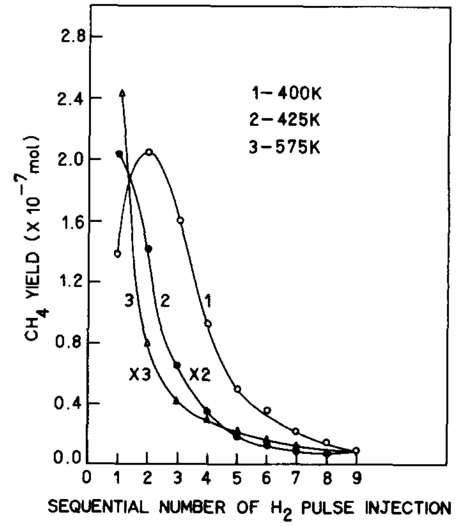


FIG. 7. CH_4 yields from the successive H_2 injections following a pulse injection of 1.52 μmol C_2H_4 over Ru/molecular sieve catalyst at different temperatures.

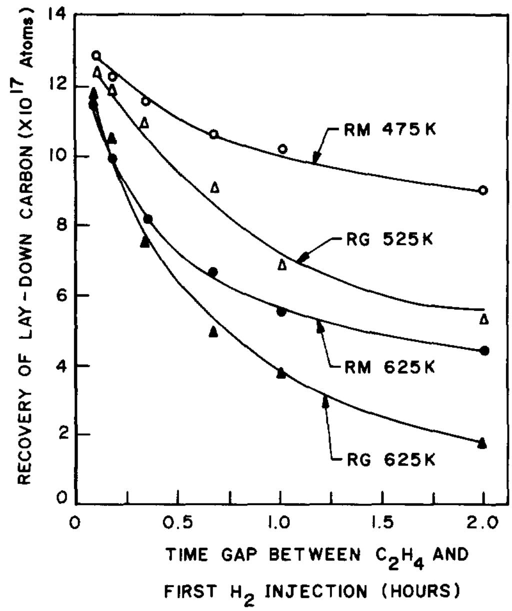


FIG. 8. Total amount of laid-down carbon recovered by way of CH_4 and C_2H_6 formation in self-hydrogenation of C_2H_4 over Ru/molecular sieves and Ru/glass beads and then in the successive hydrogen injections over the catalyst surface with varying time interval between the C_2H_4 and first hydrogen injection. Amount of C_2H_4 injected in each pulse = 1.52 μmol ≡ 18.3 × 10^{17} atoms of carbon.

two catalysts RM and RG having nearly the same metal content. The data of Fig. 8 clearly show that with increasing time and temperature, the surface carbon species become inactive for H_2 reaction. The observed steeper drop in reactivity of carbon species in the case of RG as compared to RM (Fig. 8) may be ascribed to the lower metal dispersion and surface area of the RG catalyst (Table 1).

C. Reaction on Support Materials

When C_2H_4 pulse injections were made over metal-free support materials under similar conditions as in Section A, no C_2H_6 or CH_4 was formed and a part of the C_2H_4 was found to remain adsorbed, the extent depending on temperature. Subsequent to C_2H_4 injections, when H_2 pulse injections were made (Section B), a small yield of C_2H_6 was observed from molecular sieves and alumina at temperatures above 475 K and at no stage was CH_4 found to be formed. In the case of glass beads, however, no C_2H_6 formation was observed on H_2 injections at the temperatures under investigation.

DISCUSSION

The following are the main observations of these studies:

(i) Disproportionation/self-hydrogenation of C_2H_4 occurs predominantly at Ru sites.

(ii) CH_4 formation in the interaction of C_2H_4 with the catalyst is accompanied by a reduction in C_2H_6 yields (Fig. 1) and this compares well with the CH_4 formation in the reaction of C_2H_6 over the catalyst surface (Fig. 2). Therefore, it is suggested that the interaction of C_2H_4 in the absence of H_2 results initially in the formation of C_2H_6 and hydrogen-deficient carbon species. The further disproportionation or reduction of C_2H_6 may in turn give rise to the formation of CH_4. The reducing agent could either be the surface adsorbed H_2 or the hydroxyl groups of the support material (*11*, *16*).

(iii) The data of Fig. 3 indicate the presence of unsaturated dicarbon (C_2) and monocarbon (C_1) species over catalyst surface, the former being more predominant at lower temperatures.

The data of Fig. 1 show that only a part of the chemisorbed C_2H_4 converts to C_2H_6 and/or CH_4. For example, in the case of RM catalyst at 375 K about 40% of C_2H_4 converts to C_2H_6 while at 600 K only 20% of C_2H_4 converts to CH_4 (Fig. 1A). It would therefore appear that either a part of the unreacted C_2H_4 remains chemisorbed on the catalyst surface or it becomes converted to unsaturated carbon species and H_2 via a route other than the one accompanied by its self-hydrogenation. The observed formation of H_2 in the interaction of C_2H_4, at least in the case of RG catalyst (Section IIIA), is supportive of the latter view.

(iv) The increase in CH_4 yield at 375 K with increase in time interval between C_2H_4 and first H_2 injection (Fig. 4) may occur if

(a) the intermediate species present on the support material diffuse to metal sites where they result in the formation of C_1 species (*17*), (b) the surface has more than two kinds of Ru sites (*18, 19*), the surface species possibly migrating with time from low to more energetic sites, or (c) the intermediate C_2 species undergo transformation to yield the C_1 species.

The fact that the time-dependent growth in CH_4 yield was observed even in catalysts with less porous or nonporous supports (Fig. 5) is a clear evidence in favour of $C_2 \rightarrow C_1$ transformations at the surface; however, the contribution of route (a) or (b) cannot be completely ruled out.

(v) The reduction in CH_4/C_2H_6 yields with increase in catalyst temperature and also with increase in C_2H_4–1st H_2 time interval (Figs. 4, 5, and 8) clearly show that both the C_2 and C_1 unsaturated species convert with time to an inactive form, the process being accelerated with increase in temperature. The inactivation of C_2 and C_1 species find their parallel in the formation of graphitic species in the interaction of CO over group VIII metals (*14, 20, 21*).

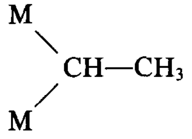
The data of Fig. 8 also show that the nature of the support material considerably influences the decay behaviour of carbon species which would in turn affect the regeneration characteristics of the catalyst.

Several modes of C_2H_4 chemisorption on group VIII metals have been proposed for both single-crystal and supported forms of catalysts. Depending on the catalyst and its temperature, exposure to C_2H_4 may initially give rise to formation of one of the following species:

(i) $M{-}CH_2{-}CH_2{-}M$ (π- or σ-diadsorbed)

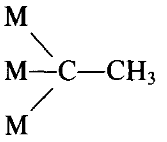
(ii) $M{-}CH{=}CH_2$ (mono adsorbed)

(iii)



(ethylidene group)

(iv)

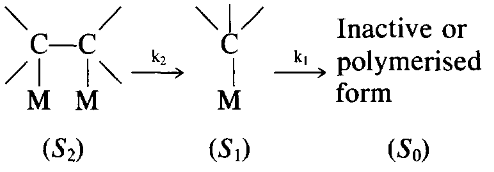


(ethylidyne group)

where M refers to the metal site.

In general, supported metal catalysts are believed to chemisorb ethylene in di-adsorbed form at low temperatures (*5, 22*), though with single crystals both di-adsorbed and ethylidene groups have been reported (*23–25*). At room temperature and above, ethylene is reported to be dissociatively adsorbed over group VIII metals both in metal and supported forms (*26*). Using a Pt/SiO_2 catalyst, Komers *et al.* (*3*) have shown that though the self-hydrogenation of C_2H_4 occurred at room temperature, a fraction of ethylene remained irreversibly adsorbed, undergoing further self-hydrogenation at 373 K and decomposing to CH_4 at about 493 K.

Thus at temperatures above 300 K, where the present studies have been carried out, no significant amount of unreacted C_2H_4 is likely to be present on the catalyst surface and hence any reaction involving C_2H_4(ads) and H(ads) would also be less probable. The principal species involved in surface reactions would therefore be the hydrogen-deficient C_2 and C_1 species and the catalyst surface model subsequent to C_2H_4 adsorption and self-hydrogenation would be



where k_2 and k_1 are the rate constants and S_2, S_1, and S_0 indicate the concentration of C_2, C_1 and the inactive carbon species.

For the time being if we consider the deactivation through only S_1 sites than at any time t,

$$S_2 = (S_2)_0 e^{-k_2 t}, \quad (1)$$

where $(S_2)_0$ is initial concentration, and

$$S_1 = \frac{k_2}{k_2 - k_1}(S_2)_0[e^{-k_1 t} - e^{-k_2 t}] + (S_1)_0 e^{-k_1 t}. \quad (2)$$

Taking C_2H_6 yields as a measure of S_2 concentration, the semilog plots of C_2H_6 yield vs C_2H_4–1st H_2 time gap indicate the existence of a two-stage process. The k_2 values for the initial (faster) stage were estimated as 0.02, 0.035, and 0.08 min^{-1} at 375, 425, and 475 K, respectively, which gave an activation energy (E) value of ~5.4 kcal mol^{-1}. For the second (slower) stage the k_2 values were 0.009, 0.013, and 0.06 min^{-1} at 375, 425, and 475 K, respectively, the corresponding E value being ~14 kcal mol^{-1}. The two decay stages for dicarbon species indicate that these species present at different sites have varying decay rate or reactivity. Heterogeneity among the active Ru sites may explain the data of Fig. 6 where it is seen that for different C_2H_4–1st H_2 time intervals, though the yields of CH_4 and C_2H_6 differ widely for first three to four injections, subsequent H_2 injections gave almost identical yields.

Taking CH_4 yields (Fig. 4A) as a monitor of S_1, k_1 could be evaluated using Eq. (2). For example, the value of k_1 at 375 K was found to be 0.0042 min^{-1}. At higher temperatures, where step $S_2 \rightarrow S_1$ may play a negligible role, the decrease in CH_4 yield would be governed by deactivation of monocarbon species. The semilog plots of CH_4 yields versus C_2H_4–1st H_2 injection time gap (Fig. 4A) also revealed that variation of CH_4 yield follows a multistep process. This, therefore, indicates that there are at least two sources responsible for the buildup of C_1 species which may correspond to the two decay stages of C_2 species as discussed above and similarly the C_1 species present at different Ru sites may have varying rates of deactivation.

The sequential H_2 injection data of Fig. 6 are also amenable to the kinetic treatment, although more complex. The decay of S_2 in between two H_2 pulses is governed by Eq. (1). Rapid removal of S_2 and S_1 sites occurs during the short interaction time of H_2 pulse by reaction with hydrogen, viz.,

$$S_2 + H_2 \xrightarrow{k_r} C_2H_6 \quad (3)$$

$$S_1 + H_2 \xrightarrow{k_r'} CH_4 \quad (4)$$

i.e., during $\delta\tau$ of pulse time,

$$S_2 = (S_2)_\tau e^{-\{k_r[H_2]+k_2\}t}, \quad (5)$$

where $(S_2)_\tau = (S_2)_0 e^{-k_2\tau}$ and

$$(C_2H_6)_n = \frac{k_r[H_2]}{k_r[H_2] + k_2}(1 - e^{-\alpha\delta\tau}) e^{-nk_2\tau} e^{-(n-1)\alpha\delta\tau}(S_2)_0, \quad (6)$$

where $(C_2H_6)_n$ represents the C_2H_6 yield from the nth H_2 pulse,

$$\alpha = k_r[H_2] + k_2,$$

and τ is the time interval between two pulses. Equation (6) can be written as

$$(C_2H_6)_n = \text{const}\ e^{-(n-1)(k_2\tau+\alpha\delta\tau)}.$$

From the plot of $\ln(C_2H_6)$ vs $(n - 1)$, we evaluate

$$(k_2\tau + \alpha\ \delta\tau) = 0.47.$$

For a pulse interval of 4 min and $k_2 = 0.0086\ \text{min}^{-1}$ we find

$$\alpha\ \delta\tau = (k_r[H_2] + k_2)\ \delta\tau = 0.43.$$

At a flow rate of 34 ml min^{-1}, $\delta\tau = 2$ s,

$$k_r[H_2] = 0.215\ \text{s}^{-1} \quad \text{or} \quad 12.90\ \text{min}^{-1}.$$

The H_2 injection corresponds to about 15 μmol of H_2 flowing through a reaction volume of 1 ml with about 2 s residence time. From this, the reaction rate constant appears to be

$$k_r = 14\ \text{M}^{-1}\ \text{s}^{-1}.$$

The above consideration shows that the depletion of S_2 by reaction with H_2 is much larger than by its decay to S_1, e.g., about 4% of the di-carbon sites decay during the 4-min time interval between two pulses, while as much as 35% of the S_2 species react with H_2 during the short 2-s pulse time giving C_2H_6.

The fast depletion of S_2 sites due to chemical reaction with H_2 is reflected in early onset of maximum CH_4 yield at the fourth H_2 pulse injection, i.e., about 16 min after C_2H_4 was initially injected (Fig. 6A, curve 1). On the contrary, at the same temperature of 375 K, if the S_2 species were not removed by successive H_2 injections (Fig. 4A) and hence were available for the growth of S_1, the CH_4 yield (i.e., S_1 sites) was found to be growing even after 60 min (curve 1).

Quantitative treatment of methane yields due to successive H_2 pulses (Fig. 6A) becomes more complex since the depletion due to reaction of both the S_2 and S_1 species will have to be considered for each H_2 pulse injection in addition to the normal growth decay character of S_1 [Eq. (2)]. The reactivity of S_1 species with H_2 to give CH_4 could be more simply obtained by analysing the CH_4 data in Fig. 6A after neglecting the CH_4 yields from the first few H_2 pulses. For example, very few S_2 species would be available after about seven pulses and hence the contribution from these to S_1 can be ignored. Thus, using the CH_4 yields from H_2 pulses 8 to 11 (Fig. 6A) we obtain $k_r' \sim 12$ M^{-1} s^{-1}. Both the S_2 and S_1 species therefore appear to have comparable reactivity with H_2.

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