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Diffuse Reflectance FT–IR Study of the Deactivation and Reactivation of Potassium Carbonate-Supported Sodium Catalysts for Propene Dimerisation

PHILIP G. HARRISON* AND DAVID GOODYEAR

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

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Diffuse reflectance FT–IR has been used to investigate the chemical processes involved in the deactivation of Na/K_2CO_3 propene dimerisation catalysts and their reactivation by treatment with hydrogen (hydriding). The data show that deactivation of the catalyst is due to the buildup of an involatile unsaturated hydrocarbon material on the surface of the Na/K_2CO_3 catalyst. The deactivating hydrocarbon material is removed from the deactivated catalyst by hydriding at elevated temperatures, the rate of removal increasing with temperature. Hydriding initially produces propene, some of which subsequently undergoes hydrogenation to propane. Deuteriding produces a partially deuterated propene, which is converted to a partially deuterated propane with time. The origin of the deactivating hydrocarbon material is probably by polymerisation of the equilibrium mixture of methyl acetylene and allene, which are formed by secondary processes during the dimerisation of propene. Breakdown of the polymer backbone appears to be the process by which propene is formed during hydriding.

INTRODUCTION

The original discovery by Schramm (*1*) that propene undergoes dimerisation to 4-methyl-1-pentene (4MP1) in yields of 70–80% in contact with potassium, rubidium, or caesium dispersed in a hydrocarbon solvent has led to the development of highly active catalysts with good specificity for the formation of 4MP1 (80–90% specificity at a constant conversion of approximately 30% per pass) (*2*, *3*). Although the activity of hydrocarbon dispersions of the alkali metals for the dimerisation of propene to 4MP1 follows the order Cs ≈ Rb ≈ K >> Na > Li, elemental sodium supported on anhydrous potassium carbonate exhibits an activity similar to that of elemental potassium on the same support. Hence the former is used commercially, and the process operates at temperatures of ca. 420 K and pressures of 68–80 atm (4). During the working lifetime of the catalyst, both physical and chemical deactivation of the catalysts occurs (*4*). Physical deactivation is caused by the elution of sodium and potassium from the catalyst, and little can be done to prevent this phenomenon. However, the chemical deactivation can, at least in part, be reduced if not eliminated. One method of prolonging catalyst lifetime is to "prehydride" the catalyst (i.e., treat the catalyst with molecular hydrogen) prior to use and to hydride again as the deactivation occurs. This process restores catalytic activity essentially to the original level. However, little is known concerning either the mechanism of catalyst deactivation or the effect of hydriding, partly because of the difficulty in investigating these highly air-sensitive, opaque metallic grey catalyst materials. Infrared spectroscopy has been employed with great effect in the elucidation of the surface chemistry in many systems involving metal oxides, but unfortunately in the present case the opacity of the catalyst precludes the application of normal transmission optical geometry infrared studies. In contrast, diffuse reflectance

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* To whom correspondence should be addressed.

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FT-IR (DRIFT) spectroscopy offers significant potential for such difficult cases, and in this paper we report the results of a DRIFT study of several features of the Na/K_2CO_3–propene system including (i) the nature of the catalyst, (ii) the process of catalyst deactivation, (iii) catalyst reactivation by hydriding, and (iv) the interaction of propene with the catalyst.

EXPERIMENTAL

Infrared Measurements

DRIFT spectra were recorded using a Nicolet Instruments 5DXB spectrometer together with a Barnes/Spectratech diffuse reflectance accessory fitted with a controlled environment chamber. Spectra of the surface of the carbonate samples are presented in Kubelka–Munk units, whilst those in which gas phase components are of primary interest are in units of absorbance.

Preparation of the Potassium Carbonate-Supported Sodium Catalysts

Potassium carbonate (ca. 20 g) was placed in a 250-ml three-necked flask and dried under vacuum (10^{-3} Torr) at 623 K overnight. After cooling (still under vacuum), the flask was transferred to an argon-filled glove box and the required amount of clean sodium (2–20 wt%) was added in small pieces to the anhydrous carbonate. The flask was then sealed, placed in a furnace, connected to a flow of dry nitrogen, and heated slowly with stirring to 673 K, the temperature at which it was kept for 6–8 h.

Preparation of the Deactivated and Hydrided Catalysts

In an experiment carried out at BP (Chemicals) Ltd., Salt End, Hull, propene was dimerised to 4MP1 over a 4.5 wt% Na/K_2CO_3 catalyst. After charging with catalyst (88.5 g), the unit was started up by pumping through the propene feed (190 ml/h) at ambient temperature and 1000 psi. The reactor was heated to 393 K over a period of 1 h and was then heated slowly (3 K/h) to 438 K. The first sign of reaction product occurred 6 h later, and after 52 h sampling and analysis of the product commenced. The process variables were recorded hourly, and product and off gases were analysed by GLC every 4 h. When the productivity of the catalyst appeared to be falling because of deactivation (after 112 h), the unit was shut down and the reactor was removed under a nitrogen blanket, returned to a nitrogen glove box, and a sample of the deactivated catalyst obtained. The black deactivated catalyst was hydrided by passing hydrogen over it at 433 K for 16 h. Once again, the reactor was cooled and transferred to the glove box, where a sample of hydrided catalyst, which was now red/brown in appearance) was taken. The reactor was again returned to the unit and restarted using propene feed as before to produce 4MP1. After a further 18 h the experiment was terminated and a final sample of the catalyst (also black in appearance) was taken. The four catalyst samples, original, deactivated, hydrided, and used hydrided, were stored under nitrogen prior to study by DRIFT.

DRIFT Spectroscopy of Anhydrous Sodium, Potassium, and Rubidium Carbonates and of the Potassium Carbonate-Supported Sodium Catalyst

DRIFT spectra of the ground alkali metal carbonates were recorded at 393 K under vacuum (10^{-4}–10^{-5} Torr) in a controlled environment chamber attached to the diffuse reflectance accessory. DRIFT spectra of the catalyst samples were obtained by loading a sample into the controlled environment chamber in an argon-filled glove box prior to transfer of the chamber to the diffuse accessory unit. Once in position, the chamber was connected to the vacuum line system and evacuated (10^{-4}–10^{-5} Torr). Initial spectra were recorded (1000 scans, 4 cm^{-1} resolution) before any reactant gas (propene, hydrogen, or deuterium) was admitted to the chamber and the chamber was heated to the desired temperature. Spectra (100–1000 scans, 4 cm^{-1} resolution) were recorded at appropriate intervals.

TABLE 1

DRIFT and Transmission[a] Infrared Spectra of Na_2CO_3, K_2CO_3, and Rb_2CO_3 (cm^{-1})

Na_2CO_3		K_2CO_3		Rb_2CO_3	
DRIFT	Transmission	DRIFT	Transmission	DRIFT	Assignment
4250w		4160w		4130	
3920w		3850w		3820w	
3560w		3500w		3465w	$2(\nu_1 + \nu_3)$
3180w		3140w			$(\nu_1 + \nu_3) + \nu_4$
2955m	2930vw	2882m		2840m	$2\nu_4$
2851m		2801m		2780m	$2\nu_4$
2581m	2560vw	2521m	2520vw	2490m	$\nu_1 + \nu_4$
2492m	2494w	2450m	2445w	2427m	$\nu_1 + \nu_4$
2118w	2120vvw	2083w	2083vvw	2064w	$\nu_3 + \nu_4$
1777s	1776w	1749m	1751w	1734s	$\nu_1 + \nu_3$
	1451vs		1421vs		ν_4
1078w	1079vvw		1060vvw	1051vw	ν_1
887m	881s	882m	880m	880m	ν_2
855m	855w	855w	855vw	853w	
700m	701w	689m	691w		ν_3
693m	694w		685w	683m	ν_3
				667w	

[a] Reference (*5*).

RESULTS

DRIFT Spectra of Anhydrous Sodium, Potassium, and Rubidium Carbonates and of the Potassium Carbonate-Supported Sodium Catalyst

The DRIFT spectra of all three alkali metal carbonates were similar in form (Table 1 and Fig. 1) but differ from the absorption spectra in that the ν_4 band, which is present as the most intense feature of the absorption spectra (*5, 6*), appears to be absent. This is due to band inversion (anomalous dispersion or the reststrahlen effect (*7*)) caused by the contribution of the specularly reflected radiation from the particles on the top layer of the sample, which does not penetrate into the bulk of the sample. As a result, the intense ν_4 band is not observed; rather, the 1600–1300 cm^{-1} region of the DRIFT spectra is invalid. Although this effect could have been removed by mixing with a diluent (which would have afforded a DRIFT spectrum with the same appearance as a typical absorption spectrum), this was not done in the present study for two reasons: (a) the combination bands and overtones that occur above 2400 cm^{-1}, which are characteristic for each alkali metal carbonate, are well defined in the undiluted spectra, and (b) the surface of the Na/K_2CO_3 catalysts would have been at least partly destroyed by the grinding process involved. In all three spectra, the splitting of the ν_4 band, although not observed directly, is apparent from the splitting of the $2\nu_4$ overtone and the $\nu_1 + \nu_4$ combination band. The ν_1 fundamental, activated by the lowering of symmetry due to cation–anion interaction, is observed as a weak band in the spectra of sodium (1078 cm^{-1}) and rubidium (1051 cm^{-1}) carbonates. The position of the more intense ν_2 fundamental appears to be essentially independent of the alkali metal cation at 880–887 cm^{-1}. Thus, as can be seen from the data in Table 1, both the $2\nu_4$ overtone and the $\nu_1 + \nu_4$ combination band are characteristic for each particular alkali metal carbonate, with the positions of the bands shifting monotonically to lower

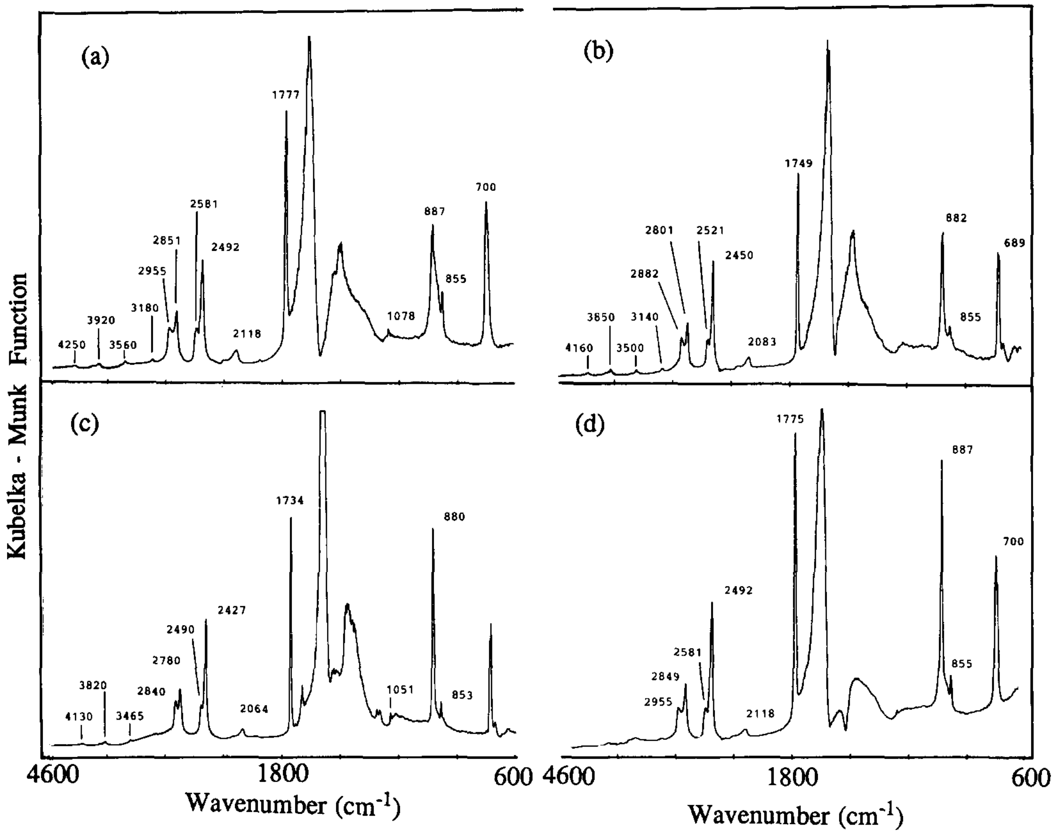


FIG. 1. DRIFT spectra of (a) Na$_2$CO$_3$, (b) K$_2$CO$_3$, (c) Rb$_2$CO$_3$, and (d) a K$_2$CO$_3$ pellet after reaction with sodium.

energy with increasing ionic radius of the metal cation.

The DRIFT spectrum of a potassium carbonate pellet was also recorded before and after reaction with sodium at 276 K for 5 h followed by removal of excess elemental sodium by distillation. The spectrum obtained (Fig. 1d) shows that after reaction the surface of the potassium carbonate particles is composed entirely of sodium carbonate, indicating that an exchange reaction occurs at the surface with the implicit formation of elemental potassium.

DRIFT Spectra of the Catalyst Samples

The DRIFT spectrum in the 2050–3200 cm^{-1} region of the 4.5 wt% Na/K$_2$CO$_3$ catalyst used for the propene dimerisation run is illustrated in Fig. 2a. Comparison with the DRIFT spectra of sodium and potassium carbonates show it to resemble closely that of potassium carbonate. However, closer examination of the $2\nu_4$ overtone region around 2900 cm^{-1} reveals a weak feature at 2953 cm^{-1} associated with sodium carbonate in addition to those characteristic of potassium carbonate at 2885 and 2801 cm^{-1}. This indicates that in the active catalyst, some Na–K$^+$ exchange has taken place, albeit incompletely, releasing some elemental potassium at the catalyst surface.

The DRIFT spectrum of the deactivated catalyst is shown in Figs. 2b and 3. Spectral subtraction of the carbonate support shows that extra bands, presumably due to a surface deactivating species, are found at 3038,

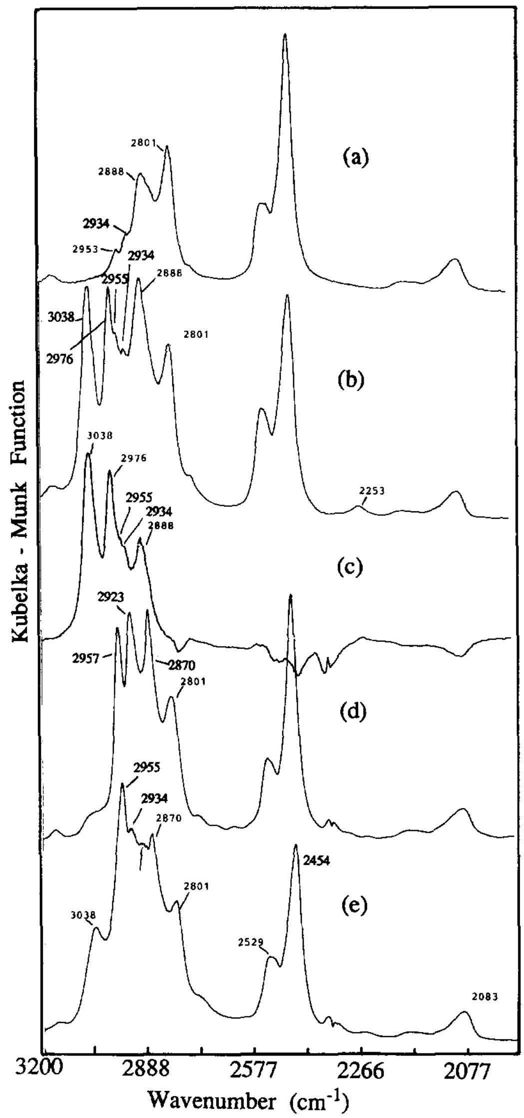


FIG. 2. DRIFT spectra of (a) the 4.5 wt% Na/K_2CO_3 catalyst used in propene dimerisation, (b) the deactivated catalyst from the reactor after propene dimerisation, (c) the deactivating surface hydrocarbon material [obtained by subtraction of (a) from (b)], (d) the hydrided catalyst, and (e) the used hydrided catalyst.

2976, 2888, 2253, 1246, 1009, and 933 cm^{-1} (Figs. 2c and 3). The position of these bands suggests that the deactivating species is an unsaturated hydrocarbon, with the band at 3038 cm^{-1} being assigned to an alkenyl C–H stretching mode and the bands at 2976 and 2888 cm^{-1} assigned to alkyl C–H stretching modes. The less-well-defined, lower intensity bands at 1246, 1009, and 933 cm^{-1} are assigned as ν(C–C) stretching and/or δ(C–H) deformation modes. The weak feature at 2253 cm^{-1} is assigned to either a combination band (1246 + 1009 = 2253 cm^{-1}) or possibly a ν(C≡C) stretching mode.

Reactivation of the deactivated catalyst by hydriding has been presumed to proceed by removing the deactivating hydrocarbon from the catalyst surface. This hypothesis is corroborated by the spectrum of the hydrided catalyst (Fig. 2d), in which the peaks at 3038, 2976, 2888 cm^{-1} and those below 1300 cm^{-1} are absent. However, the spectrum of the hydrided catalyst is not identical to that of the starting catalyst, and additional bands at 2957, 2923, and 2870 cm^{-1}, probably due to a saturated surface hydrocarbon, are also present. The corresponding deformation bands due to such a surface species will be expected to fall in the invalid 1600–1300 cm^{-1} region.

After hydriding, the catalyst was again used in the dimerisation unit, but a sample was extracted while still at peak activity. The DRIFT spectrum of this sample exhibited bands at 3038, 2955, 2934, 1246, and 1009 cm^{-1} characteristic of the deactivating unsaturated hydrocarbon material, but with intensity much lower than that observed for the fully deactivated catalyst (Fig. 2). The band expected at 2976 cm^{-1} is masked by the $2\nu_4$ overtone of the carbonate support.

Hydriding the Deactivated Catalyst

Reactivation of the deactivated catalyst by hydriding was studied *in situ* using the controlled environment chamber and infrared spectra are shown in Fig. 4. Hydrogen (620 Torr) was admitted to the chamber at ambient temperature. No change was observed in the spectrum of the catalyst surface, although weak bands due to gas phase propene (2953 and 912 cm^{-1}) appeared. No additional changes occurred after a further 2 h at ambient temperature, which was then raised to 343 K. After 1 h at 343 K, the peaks associated with the surface hydrocarbon, al-

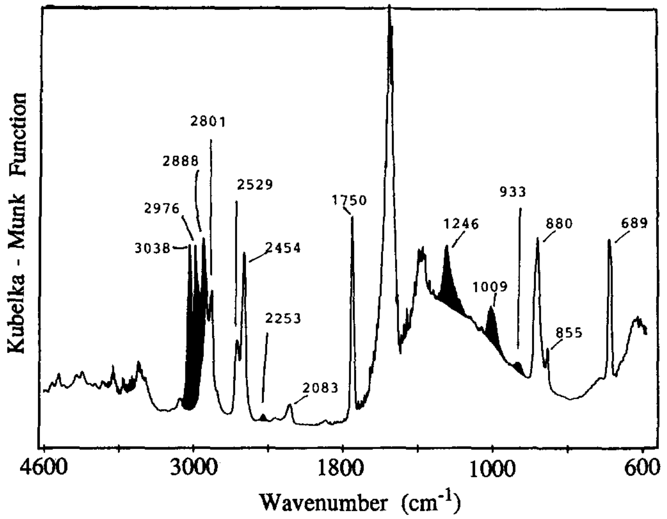


FIG. 3. DRIFT spectrum of the deactivated catalyst obtained from the reactor after propene dimerisation (bands due to the deactivating surface hydrocarbon material are shaded).

though diminished, were still present, together with gas phase bands due to propene (3102, 2955, 2932, 991, and 912 cm^{-1}) and propane (2969 cm^{-1}) (*7*). The surface hydrocarbon material was completely removed after 6 h, with propene (3102, 2955, 2932, 991, and 912 cm^{-1}) and propane (2969, 2901, 2888, and 2878 cm^{-1}) very evident in the gas phase. Continued heating at 343 K resulted in a decrease in the intensity of the propene peaks at it undergoes hydrogenation to propane (Fig. 5). The same sequence of events

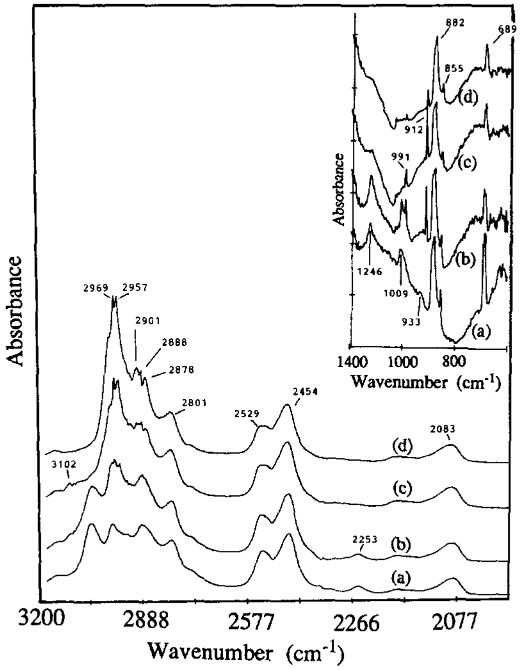


FIG. 4. Infrared spectra of the reaction between the deactivated catalyst and hydrogen at 343 K after (a) 0, (b) 1, (c) 6, and (d) 21 h.

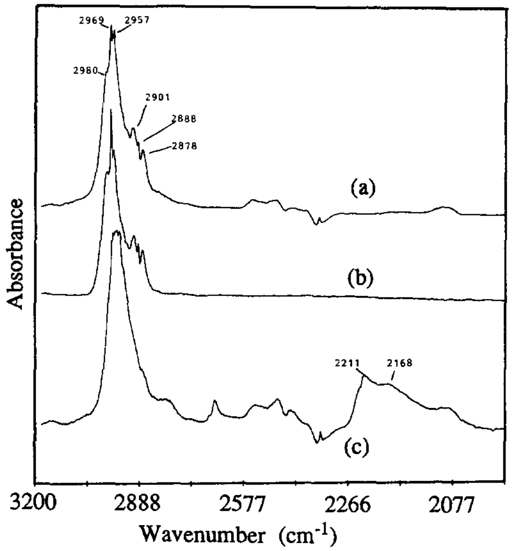


FIG. 5. Infrared spectra of (a) the gas phase at the end of the reaction between the deactivated catalyst and hydrogen at 343 K, (b) propane, and (c) the gas phase at the end of the reaction between the deactivated catalyst and deuterium at 388 K.

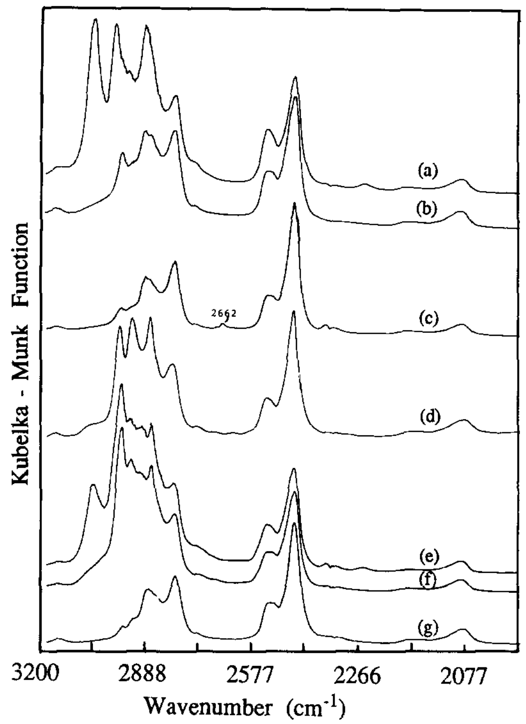


FIG. 6. DRIFT spectra of (a) the start and (b) the end of the reaction between the deactivated catalyst and hydrogen at 343 K. The corresponding DRIFT spectrum taken at the end of the reaction between the deactivated catalyst and deuterium is shown in (c). The DRIFT spectrum of the industrially hydrided catalyst is shown in (d), together with those recorded at (e) the start and (f) the end of the reaction between the used-hydrided catalyst and hydrogen at 345 K. The DRIFT spectrum of the starting catalyst is shown in (g).

was observed when the deactivated catalyst was hydrided in the environmental chamber at temperatures >343 K, but at a much faster rate (e.g., at 458 K, the surface hydrocarbon material is removed after only 10 min).

DRIFT spectra of the surface of the deactivated catalyst at the start and end of the hydriding reaction, together with those of the original and industrially hydrided catalyst are shown in Fig. 6. This shows that the surface of the laboratory-hydrided catalyst is similar to that of the original catalyst, but differs somewhat from the industrially hydrided catalyst. The laboratory-hydrided catalyst exhibits an increase in the intensity of the 2955 cm^{-1} band over the original catalyst, and a weak band is observed at 2870 cm^{-1}, but the change in surface is not as severe as that seen in the industrially hydrided catalyst.

Deuteriding the Deactivated Catalyst

In a similar experiment, the deactivated catalyst was deuterided (580 Torr) (spectra are shown in Fig. 7). No reaction was observed at ambient temperature. However, after 1 h at 388 K, bands characteristic of the surface hydrocarbon material were greatly reduced in intensity, and propene (3104, 2953, 2932, and 912 cm^{-1}) was seen in the gas phase. The surface hydrocarbon material was removed completely within 4 h, and a deuterated gas phase hydrocarbon was observed with bands at 2211 and 2168 cm^{-1}. The peaks grew with time and are ascribed to a deuterated propane, which is possibly formed initially with propene and subse-

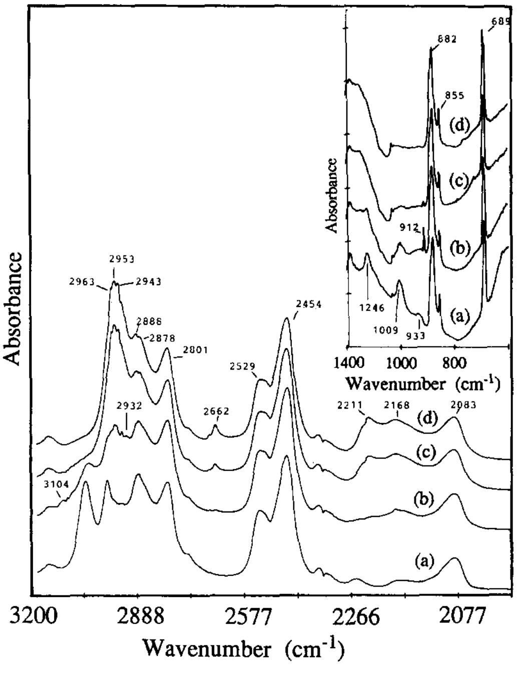


FIG. 7. Infrared spectra of the reaction between the deactivated catalyst and deuterium at 388 K after (a) 0, (b) 1, (c) 4, and (d) 26 h.

quently as the propene produced is deuterated. The production and loss of propene can best be followed by the appearance and loss of the band at 912 cm^{-1}. After 26 h no propene is apparent in the spectrum, and subtraction of the original catalyst spectrum affords a broad, poorly defined band centered at ca. 2950 cm^{-1}, which is attributed to partially deuterated propane (Fig. 5c). After removal of the surface hydrocarbon material, the catalyst surface is very similar to that of the original catalyst, apart from a previously unobserved band at 2662 cm^{-1} (Figs. 6c and 6g). This weak band, which grows in intensity during the course of the reaction, did not disappear upon evacuation of the gaseous products and is therefore associated with the catalyst surface. The origin of this weak band is not due to a surface OD species since it is also observed on treating the original catalyst with either hydrogen or deuterium at 423 K. It is possible that it is an overtone band due to the Na_2CO_3 support (e.g., $3\nu_2 = 2661$ cm^{-1}). As with the reaction with hydrogen, increasing the temperature to 458 K resulted in the complete removal of the surface hydrocarbon material within 10 min.

Hydriding the Used Hydrided Catalyst

Removal of the lower level of the surface hydrocarbon material present on the used hydrided catalyst was complete after only 30 min at 345 K with 650 Torr of hydrogen. Propene and possibly propane are initially formed in the gas phase. Only the latter is present in the gas phase after 20 h. Removal of the surface hydrocarbon material produces a surface very similar to that of the industrially hydrided catalyst (Fig. 6d and 6f).

Deuteriding the Used Hydrided Catalyst

In a similar experiment using deuterium (680 Torr), the surface hydrocarbon material was completely removed after 50 min at 378 K. Poorly resolved peaks due to deuterated propene/propane are observed at 2211 and 2168 cm^{-1} and propene at 912 cm^{-1}. Since the latter band is absent after 270 h, the two bands at 2211 and 2168 cm^{-1} that still remain are attributed to a deuterated propane. The catalyst surface at the end of the treatment resembles that of the industrially hydrided catalyst, and again a weak band is observed at 2662 cm^{-1}.

Behaviour of Propene over the Original Catalyst

A sample of the fresh 4.5 wt% Na/K_2CO_3 catalyst used in propene dimerisation was reacted with propene (250 Torr, 373 K) in the controlled environment chamber for 220 h. No evidence of the dimerisation product was apparent after this time, but propane was observed in the gas phase after 89 h. When the experiment was repeated at 458 K the reaction proceeded somewhat faster, and propane was observed after 260 min and increased with time. No dimerisation product or hydrocarbon material was observed.

Behaviour of Propene over the Industrially Hydrided Catalyst

The industrially hydrided catalyst, which had shown a greater reactivity towards propene than the original catalyst towards propene dimerisation, was reacted with propene (260 Torr, 458 K) in the controlled environment chamber. No reaction was observed at ambient temperature, but at 458 K only propane was formed.

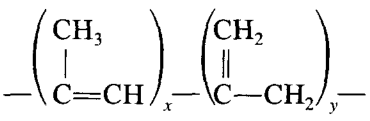
DISCUSSION

The data show that an involatile unsaturated hydrocarbon material (bands at 3038, 2976, 2888, 2253, 1246, 1009, and 933 cm^{-1}) is present on the surface of the deactivated Na/K_2CO_3 catalyst and that it can be removed to varying degrees by the process of hydriding at elevated temperatures. That this material is responsible for the deactivation is demonstrated by the catalyst reactivation upon its removal from the surface by hydriding. The deactivating material is also present on the used hydrided catalyst but to a lesser extent since the used hydrided catalyst was employed in the catalytic dimerisation for a much shorter period of time. Thus, it would appear that deactivation of the catalyst results from a cumulative buildup of hydrocarbon material on the catalyst surface. That the material is oligomeric or polymeric in nature is indicated by its insolubility (it cannot be washed from the catalyst) and involatility (it cannot be removed by heating *in vacuo* (10^{-4} Torr) at 393 K for 24 h).

The spectra of the hydrided catalyst show the loss of bands associated with the surface hydrocarbon material, indicating that industrial hydriding of the deactivated catalyst removes the deactivating hydrocarbon material producing a reactivated catalyst. However, the spectrum of the industrially hydrided catalyst is not the same as that of the starting catalyst in the region >2800 cm^{-1} and exhibits new bands at 2957, 2923, and 2870 cm^{-1}, indicating that some of the surface hydrocarbon material is only hydrogenated to polymeric saturated hydrocarbon rather than removed completely from the surface of the catalyst.

The deactivating surface hydrocarbon material is removed from the deactivated catalyst and the used hydrided catalyst both by hydriding and deuteriding under laboratory conditions. The rate of removal of the surface hydrocarbon material increases with temperature, and in general the reaction is faster with hydrogen than with deuterium. The hydriding experiments also produced much better defined spectra. Hydriding initially produced propene (bands at 3104, 2955, 2932, 991, and 912 cm^{-1}), although the initial formation of very small amounts of propane cannot be excluded. Subsequently the gas phase comprised both propene and propane (bands at 2969, 2901, 2888, and 2878 cm^{-1}), most probably formed by hydrogenation of propene. Similarly, deuteriding produced a partially deuterated propene (bands at 3104, 2955, 2932, and 912 cm^{-1}), which is converted to a partially deuterated propane (bands at 2950, 2211, and 2168 cm^{-1}) with time. The two bands observed at 991 and 912 cm^{-1} in the spectrum of propene are the out-of-plane deformation modes of the $-CH=$ and CH_2 groups, respectively. The fact that the band at 991 cm^{-1} is absent from the spectrum of the partially deuterated propene obtained in the deuteriding experiments whereas the 912 cm^{-1} band is present would suggest strongly that deuteration occurs during deuteriding to afford a propene with a $-CD=CH_2$ unit.

The observation that only propene and propane are formed as gas phase products during the hydriding process implies that the deactivating material on the catalyst surface is formed by polymerisation of C_3 units. The origin of the deactivating hydrocarbon material is probably polymerisation of the equilibrium mixture of methyl acetylene and allene, which are formed by secondary processes during the dimerisation of propene, giving a polymer of the form (*4*)



$$-\left(\overset{\overset{\displaystyle CH_3}{|}}{C}=CH\right)_x-\left(\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2\right)_y-$$

Homopolymers of both methyl acetylene (*9*, *10*) and allene (*11*) have been prepared and are dark in colour, but unfortunately infrared spectra are not available and so a comparison with the deactivating material in this study is not possible. Hydriding of such a polymer would lead to the formation of propene, whilst hydrogenation of the C–C bonds would lead to a saturated hydrocarbon polymer as observed on the surface of the used hydrided catalyst. Deuteriding would lead to the formation of $CH_3CD=CHD$ and $CH_2DCD=CH_2$ from the methyl alkynyl and allenyl fragments of the polymer, respectively. Thus, since deuteriding produces a propene molecule possessing a $-CH=CH_2$ unit, it would appear that the polymer comprises a poly(allenyl) structure.

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