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Studies of Adsorption and Thermal Desorption of Ethene and Propyne over Rhodium Catalysts

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The adsorption and thermal desorption of ethene and propyne, over rhodium trichloride/silica, rhodium nitrate/silica, and rhodium oxide/silica catalysts, has been studied. After reduction the nitrate- and oxide-derived catalysts were found to have retained hydrogen which was reactive to the adsorbing gases. The amount of hydrocarbon adsorbed on these two catalysts was significantly greater than that adsorbed on the chloride-derived catalyst, as were the amounts of hydrocarbon retained. Carbon monoxide and oxygen were used as probe molecules and showed that the catalyst as well as the adsorbed hydrocarbon affect the reactivity of the hydrocarbonaceous deposit. © 1986 Academic Press, Inc.

INTRODUCTION

In a previous paper on carbon monoxide adsorption (*1*), we showed that different adsorption and desorption behaviour could be observed between catalysts with the same metal and support but starting from different metal salts. To investigate whether the same type of effect would be seen when the adsorbate was an unsaturated hydrocarbon, we have studied the adsorption of ethene and propyne over three rhodium catalysts. Over the last 3 decades there has been a considerable amount of research into the adsorption of unsaturated hydrocarbons onto Group VIII metals (*2*) with ethene and ethyne being the two most thoroughly studied: to the best of our knowledged propyne chemisorption has not been studied previously. When ethene is adsorbed on Group VIII metals a significant proportion is retained (*3*); for example, anything between 64% for palladium and 7% for platinum may be retained. The retention of a hydrocarbonaceous species is, for ethene, almost certainly linked to dissociative adsorption. The amount of dissociative chemisorption varies from metal to metal and is also temperature dependent (*4*). To investigate the retained material, carbon monoxide and oxygen were used as probe molecules to study the reactivity and site blocking ability of the deposits.

The method of adsorption and desorption has been used by us previously (*1*) and was shown to be most revealing. Adsorption is immediately followed by thermal desorption up to a temperature of 573 K: this temperature was chosen so as to achieve as high a temperature as possible without exceeding the reduction temperature. Immediately after the thermal desorption the catalysts are cooled and the adsorption repeated with no intermediate treatment of the catalysts. This sequence usually results in material being retained by the catalyst but often this gives a more realistic system, compared to a working catalyst, than the initial clean metal surface.

EXPERIMENTAL

The apparatus used throughout this study was a pulse-flow microreactor system. Using this system, the catalysts could be activated in flowing hydrogen, maintained in flowing helium and then covered by the adsorbate gas by injecting pulses of known size into the helium carrier-gas stream and

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hence to the catalyst. The amount of gas adsorbed, from any pulse, was determined from the difference between a calibration peak area and the peak area obtained following the injection of pulses of comparable size onto the catalyst. Adsorptions and desorptions were followed using a gas chromatograph equipped with a thermal conductivity detector and coupled to a mass spectrometer (Spectramass SM100D).

Three catalysts were used in this study: rhodium trichloride/silica, rhodium nitrate/silica, and rhodium oxide/silica. The rhodium trichloride and nitrate catalysts were prepared by adding silica (Davison 952, surface area 280 $m^2 g^{-1}$) to an aqueous solution of the compound and evaporating to dryness. The rhodium oxide catalyst was prepared by heating a rhodium nitrate/silica catalyst to 723 K in flowing air (>100 $cm^3 min^{-1}$) for a period of 2 h. After the supported salt was dried, 0.50 g was placed in the reactor on a glass sinter and reduced in a flow of hydrogen (80 $cm^3 min^{-1}$) by heating to 573 K. The catalyst was cooled in flowing hydrogen and maintained in a flow of helium (80 $cm^3 min^{-1}$). The reduced catalysts were examined by ESCA; no residual counterions or valency states of the metal greater than zero were detected. The dispersion was measured by carbon monoxide chemisorption, assuming a CO : Rh ratio of 1 : 1, as 66% for $RhCl_3$/silica, 82% for $Rh(NO_3)_3$/silica, 85% for 1.6% Rh_2O_3/silica, and 98% for 0.9% Rh_2O_3/silica. Pulses (4 cm^3 volume, 6.67×10^3 to 2.00×10^4 Pa pressure) of the adsorbate gas were passed over the catalyst at 293 K until adsorption was complete; then the catalyst was heated in flowing helium to 573 K at 100 K min^{-1} and the desorption noted. The catalyst was then cooled in flowing helium and the adsorption/desorption cycle repeated.

Both the helium (B.O.C. 99.998%) and the hydrogen (B.O.C. 99.9998%) were further purified by passing through an activated palladium bronze to remove any oxygen impurity and a bed of soda asbestos to remove any water impurity. The ethene and propyne (both BDH 99.8 and 96.5%, respectively) were used as received.

RESULTS

Ethene Adsorption and Desorption

Pulses of ethene, at 3.0-min intervals, were passed over each of the catalysts immediately after reduction. In each case self-hydrogenation of ethene to ethane was observed; no other product was detected. Table 1 shows a pulse by pulse analysis of the adsorptions. The total amount of ethene adsorbed was 87.28 μmol (g · catalyst)$^{-1}$ for rhodium nitrate/silica (giving a C_2H_4 : Rh ratio of 1 : 1), 72.56 μmol (g · catalyst)$^{-1}$ for rhodium oxide/silica (giving a C_2H_4 : Rh ratio of 0.8 : 1), and 43.70 μmol (g · catalyst)$^{-1}$ for rhodium chloride/silica (giving a C_2H_4 : Rh ratio of 0.3 : 1). The amount of ethene adsorbed on successive chemisorption cycles decreases to steady-state values shown in Table 2. We define the steady state as having been reached when two successive adsorptions are identical.

Once saturated with ethene the catalysts were heated from 293 to 573 K at a rate of ~100 K min^{-1} in the helium gas stream and the desorption products were passed through the gas chromatograph and mass spectrometer. The species which were desorbed are detailed in Table 3. Clearly very little of the adsorbed material is desorbed from either the initial chemisorption or steady-state chemisorptions. The production of carbon dioxide from the thermal desorption over the chloride-derived catalyst was not totally unexpected. From previous studies (*1*) we have shown that there is considerable water retained by the support, when the catalyst is prepared from rhodium trichloride, which will react with adsorbed carbon to form carbon dioxide under thermal desorption conditions.

Propyne Adsorption and Desorption

Pulses of propyne, at 4.5-min intervals, were passed over the catalysts immediately

TABLE 1

Pulse Analysis of Initial Ethene Adsorptions

Catalyst[a]	% Rh[b]	Pulse No.	Amount of ethene[c]		Ethane produced[c]	Residual species[d]	Hydrogen required[e]
			In pulse	Ads.			
$Rh(NO_3)_3/SiO_2$	0.9	1	14.33	0.26	14.07	C_2H_0	27.08
		2	14.25	2.31	11.94	C_2H_0	14.65
		3	14.19	2.57	11.61	C_2H_0	12.92
		4	14.11	4.70	9.42	C_2H_0	0.0
		5	14.03	4.68	9.35	C_2H_0	0.0
		6	13.95	5.75	8.21	$C_2H_{1.1}$	0.0
		7	13.86	5.76	8.09	$C_2H_{1.2}$	0.0
		8	13.78	5.96	7.82	$C_2H_{1.4}$	0.0
		9	13.73	5.45	6.86	$C_2H_{1.5}$	0.0
		10	13.67	2.49	3.44	$C_2H_{1.2}$	0.0
		11	13.62	1.93	2.41	$C_2H_{1.5}$	0.0
		12	13.56	1.78	2.08	$C_2H_{1.7}$	0.0
Rh_2O_3/SiO_2	0.9	1	14.11	0.0	14.11	C_2H_0	28.24
		2	14.06	0.95	13.11	C_2H_0	22.43
		3	14.00	2.23	11.78	C_2H_0	14.65
		4	13.95	2.36	11.59	C_2H_0	13.75
		5	13.89	3.57	10.32	C_2H_0	6.35
		6	13.82	4.34	9.49	C_2H_0	1.63
		7	13.75	3.44	10.32	C_2H_0	6.88
		8	13.67	3.11	10.56	C_2H_0	8.70
		9	13.60	4.40	9.20	C_2H_0	0.80
		10	13.53	4.85	7.66	$C_2H_{0.8}$	0.0
		11	13.45	3.31	3.17	$C_2H_{2.1}$	0.0
		12	13.38	1.86	1.58	$C_2H_{2.3}$	0.0
		13	13.31	1.86	1.30	$C_2H_{2.6}$	0.0
$RhCl_3/SiO_2$	1.6	1	15.43	5.15	10.28	C_2H_0	0.0
		2	15.32	5.50	8.21	$C_2H_{1.0}$	0.0
		3	15.20	2.66	4.42	$C_2H_{0.7}$	0.0
		4	15.10	2.49	3.29	$C_2H_{1.4}$	0.0
		5	15.03	2.04	2.13	$C_2H_{1.9}$	0.0
		6	14.98	1.83	1.06	$C_2H_{2.8}$	0.0
		7	14.93	2.18	0.0	C_2H_4	0.0

[a] Weight of samples 0.50 g.

[b] Units: w/w.

[c] Units: μmol.

[d] Species retained by the catalyst after hydrogen abstraction for ethane production.

[e] Amount of hydrogen (H, μmol) required to produce ethane in excess of that available from ethane.

after reduction. In each case self-hydrogenation was observed. A pulse by pulse analysis of the initial chemisorption is shown in Table 4. Certainly the most unusual aspect of these results is the formation of methane over the rhodium oxide/silica catalyst. The amounts of propyne adsorbed are 96.15 μmol (g · catalyst)$^{-1}$ for rhodium nitrate/silica (giving a CH_3CCH : Rh ratio of 1.1 : 1), 96.35 μmol (g · catalyst)$^{-1}$ for rhodium oxide/silica (giving a CH_3CCH : Rh ratio of 0.6 : 1), and 56.08 μmol (g · catalyst)$^{-1}$ for rhodium trichloride/silica (giving a CH_3CCH : Rh ratio of 0.4 : 1). The amount

TABLE 2

Steady-State Ethene Adsorptions

Catalyst[a]	% Rh[b]	Amount of[c]		Residual species[d]
		Ethene ads.	Ethane prod.	
$Rh(NO_3)_3/SiO_2$	0.9	3.80	2.94	$C_2H_{2.5}$
Rh_2O_3/SiO_2	0.9	3.39	3.75	$C_2H_{1.8}$
$RhCl_3/SiO_2$	1.6	3.01	1.38	$C_2H_{3.1}$

[a] Weight of samples 0.50 g.

[b] Units: w/w.

[c] Units: μmol. All samples were saturated after the first pulse.

[d] Species retained by the catalyst after hydrogen abstraction for ethane production.

of propyne adsorbed in the steady state is shown in Table 5.

Once saturated with propyne the catalysts were heated and the desorption noted (Table 6).

Effect of Carbon Monoxide and Oxygen Adsorption

The effect of adsorbing carbon monoxide or oxygen onto a surface precovered with ethene or propyne and vice versa is shown in Table 7. Clearly there are fundamental differences in the reactivity of the adsorbed hydrocarbon on going from one catalyst to another and one adsorbate to another.

DISCUSSION

The adsorption of ethene on rhodium/silica catalysts, prepared from rhodium trichloride, has been studied by Al-Ammar and

TABLE 3

Thermal Desorption of Ethene

Catalyst[a]	Desorption	Gas evolved	Amount desorbed[b]	Temp.
$Rh(NO_3)_3/SiO_2$	Initial	C_2H_6	6.46	388
		CH_4	5.38	398
	Steady state	C_2H_6	0.30	403
		CH_4	0.26	413
		CH_4	0.26	523
Rh_2O_3/SiO_2	Initial	C_2H_6	3.32	398
		CH_4	3.59	398
		CH_4	2.44	538
	Steady state	C_2H_6	1.01	408
		CH_4	0.45	423
		CH_4	0.70	528
$RhCl_3/SiO_2$	Initial	C_2H_6	3.07	448
		CH_4	3.80	465
		CO_2	4.20	573
	Steady state	C_2H_6	0.85	473(d)
		CH_4	0.68	488
		CO_2	1.53	573

[a] Weight of samples 0.50 g.

[b] Units: μmol.

[c] Units: K. Temperature measured at peak maximum.

[d] Shoulder on main peak at 448 K.

TABLE 4

Pulse Analysis of Initial Propyne Chemisorption

Catalyst[a]	% Rh[b]	Pulse No.	Amount of propyne[c]		Propene formed[c]	Retained species[d]
			In pulse	Ads.		
$Rh(NO_3)_3/SiO_2$	0.9	1	13.26	7.14	6.11	$C_3H_{2.3}$
		2	13.21	9.88	3.32	$C_3H_{3.3}$
		3	13.14	9.34	3.80	$C_3H_{3.2}$
		4	13.09	10.61	2.48	$C_3H_{3.5}$
		5	13.04	12.43	0.61	$C_3H_{3.9}$
		6	12.99	8.01	0.40	$C_3H_{3.9}$
Rh_2O_3/SiO_2	1.6	1	13.04	2.69	9.42	—[e]
		2	12.97	5.56	7.41	$C_3H_{1.3}$
		3	12.89	6.21	6.68	$C_3H_{1.9}$
		4	12.82	7.41	5.42	$C_3H_{2.5}$
		5	12.77	8.09	2.56	$C_3H_{3.4}$
		6	12.71	8.16	1.91	$C_3H_{3.5}$
		7	12.66	4.50	1.36	$C_3H_{3.4}$
		8	12.61	2.24	1.06	$C_3H_{3.1}$
		9	12.52	2.97	1.13	$C_3H_{3.2}$
		10	12.46	2.19	0.58	$C_3H_{3.5}$
$RhCl_3/SiO_2$	1.6	1	12.47	10.76	1.71	$C_3H_{3.7}$
		2	12.42	10.68	1.73	$C_3H_{3.7}$
		3	12.36	4.63	0.60	$C_3H_{3.7}$
		4	12.31	1.96	0.0	C_3H_4

[a] Weight of samples 0.50 g.

[b] Units: w/w.

[c] Units: μmol.

[d] Species retained by the catalyst after hydrogen abstraction for propene formation.

[e] 1.86 μmol of methane were also formed when this pulse of propyne was passed over the catalyst.

Webb (*5*). In these studies self-hydrogenation was observed and the residue was found to have an average composition of $C_2H_{3.1}$ (*6*). Given the difference in the systems and the method of adsorption (static vs pulse flow) the agreement between this

TABLE 5

Steady-State Propyne Adsorptions

Catalyst[a]	% Rh[b]	Amount of		Residual species[d]
		Propyne ads.	Propene prod.	
$Rh(NO_3)_3/SiO_2$	0.9	7.46	—[d]	C_3H_4
Rh_2O_3/SiO_2	1.6	4.07	—	C_3H_4
$RhCl_3/SiO_2$	1.6	8.09	—	C_3H_4

[a] Weight of samples 0.50 g.

[b] Units: w/w.

[c] Units: μmol. All samples were saturated after the first pulse.

[d] No propene was detected.

TABLE 6

Thermal Desorption of Propyne

Catalyst[a]	Desorption	Gas evolved	Amount desorbed[b]	Temp.[c]
$Rh(NO_3)_3/SiO_2$	Initial	C_3H_6	1.71	398
		C_2H_4	1.88	473
		CH_4	3.46	573
	Steady state	—[d]	—	—
Rh_2O_3/SiO_2	Initial	CH_4	9.32	573
		C_2H_4	3.75	—[e]
		C_3H_6	4.47	—[e]
	Steady state	CH_4	0.37	573
		C_2H_4	1.20	—[e]
		C_3H_6	0.40	—[e]
$RhCl_3/SiO_2$	Initial	CH_4	0.33	573
		CO_2	5.21	—[e]
		C_3H_6	0.67	—[e]
		C_3H_8	1.66	—[e]
	Steady state	CO_2	2.76	—[e]
		C_3H_6	0.20	—[e]

[a] Weight of samples 0.50 g.

[b] Units: μmol.

[c] Units: K.

[d] Desorbed amounts below detection level.

[e] Effluent gas stream was passed through a trap at 78 K until the maximum desorption temperature (573 K) was reached; the trap was then heated and the desorbed gases analysed.

figure and our value of $C_2H_{3.1}$, for the steady-state adsorptions, is excellent. An assumption made in the studies by Al-Ammar and Webb (5) is that there is little or no hydrogen retained by the catalyst; for the case of rhodium/silica derived from rhodium trichloride this is a reasonable assumption. However, from Table 1 it is clear that this assumption does not hold for catalysts prepared from rhodium nitrate or rhodium oxide; with both these catalysts there is a significant amount of hydrogen retained after reduction, namely Rh:H ratios of 1:2.5 and 1:1.25 for the oxide-derived and nitrate-derived material, respectively. These amounts of retained hydrogen are not unrealistic when the metal dispersion is high, as is the case with the nitrate- and oxide-derived samples. The effect of this hydrogen is apparently twofold, (i) to increase the amount of hydrogenation, and (ii) to increase the amount adsorbed. The increase in the rate of hydrogenation may at first seem trivial but some comment is called for. The initial effect of the increased rate is to suppress adsorption (this suppression of adsorption of ethene on a hydrogen precovered catalyst has been observed before (5)); no ethene was adsorbed from the first pulse when the catalyst was rhodium oxide/silica whereas almost the maximum in uptake was observed from the first pulse over rhodium trichloride/silica. In fact what we are observing is an example of the effect of a positive hydrogen pressure dependency in the rate equation (7). The second effect, that of increasing the total amount of ethene adsorbed, raises fundamental questions about the adsorbed species. The ratio for adsorption, on a fresh rhodium trichloride/silica catalyst, of ethene to carbon monoxide was 0.43:1;

TABLE 7

Adsorption of Carbon Monoxide and Oxygen on Ethene- and Propyne-Covered Surfaces

Catalyst[a]	% Rh[b]	Preads.		Secondary ads.		Displacement	
		Gas	Amount[c]	Gas	Amount[c]	Gas	Amount[c]
$Rh(NO_3)_3/SiO_2$	0.9	C_2H_4	3.72	CO	15.10	C_2H_4	0.58
						CO_2	0.15
		C_2H_4	3.72	O_2	7.26	CO_2	12.26
		CO	10.07	C_2H_4	0.45	—	0.00
		O_2	—[d]	C_2H_4	0.80	—	0.00
		CH_3CCH	7.46	CO	3.14	—	0.00
		CH_3CCH	7.46	O_2	2.01	—	0.00
		CO	6.83	CH_3CCH	3.95	—	0.00
		O_2	7.08	CH_3CCH	9.70	—	0.00
Rh_2O_3/SiO_2	0.9	C_2H_4	3.39	CO	17.04	C_2H_4	0.47
						CO_2	0.13
		C_2H_4	3.39	O_2	10.03	CO_2	13.42
		CO	18.17	C_2H_4	0.32	—	0.00
		O_2	18.82	C_2H_4	0.35	—	0.00
	1.6	CH_3CCH	4.07	CO	4.73	—	0.00
		CH_3CCH	4.07	O_2	2.74	—	0.00
		CO	9.97	CH_3CCH	2.06	—	0.00
		O_2	10.98	CH_3CCH	3.50	—	0.00
$RhCl_3/SiO_2$	1.6	C_2H_4	3.01	CO	16.89	C_2H_4	1.01
						CO_2	1.18
		C_2H_4	3.01	O_2	1.78	—	0.00
		CO	17.68	C_2H_4	0.35	—	0.00
		O_2	8.36	C_2H_4	0.37	—	0.00
		CH_3CCH	8.09	CO	2.52	—	0.00
		CH_3CCH	8.09	O_2	2.01	—	0.00
		CO	7.48	CH_3CCH	3.27	—	0.00
		O_2	4.62	CH_3CCH	5.27	—	0.00

[a] Weight of samples 0.50 g.
[b] Units: w/w.
[c] Units: μmol.
[d] Not measured.

this is typical of random two-site adsorption of ethene and a similar ratio has been observed by other workers (*5*). However, the ratios obtained from the oxide- and nitrate-derived catalysts are 1 : 1. Clearly in these cases random two-site adsorption is not a good model for ethene adsorption. The question then arises as to what is a good model for ethene adsorption on these catalysts. At present we cannot be unequivocal about the mode of adsorption and therefore we offer the following hypothesis more for discussion rather than dogmatism. To achieve such a high ethene to rhodium ratio single site adsorption is required or two-site adsorption followed by migration and/or rearrangement. Somorjai and coworkers (*8*) have studied the adsorption of ethene on rhodium single crystals and on decomposition have detected a range of species, many of which are bonded end-on to the metal. Under conditions where we are observing hydrogenation the formation of such species is not unreasonable. During thermal desorption species such as found by Somorjai *et al.* (CH, C_2, C_2H, CH_2, and CCH_3) are all likely to be formed; however, in the course of the adsorption/desorption cycles the catalyst retains material far in excess of a monolayer. For this to occur we believe that the retained species polymerise to give long-chain hydrocarbonaceous species attached to a metal site in a linear fashion, e.g., $*{=}C{-}R$; in this way there can be continual loss of adsorbate with no loss in free metal area. Similar proposals have been made for other systems (*9*). In the steady state the amount of ethene adsorbed is dramatically reduced to between 9 and 14% of the original adsorption. This reduction and the similarity between the figures suggests that ethene adsorption on the rhodium oxide and nitrate catalysts may now be similar to that of the rhodium trichloride catalyst, i.e., random two-site adsorption. This view is reinforced by the ethene to carbon monoxide ratios in the steady state, 0.4 : 1 for the nitrate, 0.2 : 1 for the oxide, and 0.2 : 1 for the chloride. Even so, ethane is still produced and it is interesting to note that the ratio of ethene adsorbed to ethane produced gives the same order as with the initial adsorption.

When the steady-state catalysts were precovered with ethene and carbon monoxide was adsorbed, the full steady-state amount of carbon monoxide was taken up even though only a small portion of the adsorbed ethene was displaced. When the experiment was reversed, only a small amount of ethene was adsorbed and no carbon monoxide was displaced. Clearly carbon monoxide blocks the ethene adsorption sites; however, ethene does not block carbon monoxide sites. An interpretation of these results which is in keeping with the discussion so far is as follows. The blocking of the ethene adsorption sites by carbon monoxide is not unexpected; carbon monoxide will pack on the surface to allow only a very small proportion of unoccupied sites. However, when ethene is preadsorbed the situation is significantly different; with random two-site adsorption approximately 14% of the sites are available for single-site adsorption (*10*) and therefore carbon monoxide can adsorb initially on these sites. On adsorption the heat of adsorption for carbon monoxide is released which supplies sufficient energy to allow desorption of the small amount of ethene, which was adsorbed as ethene. As more carbon monoxide is adsorbed and energy released the remaining hydrogen-deficient adsorbed ethene can migrate to, and be incorporated in, the already present hydrocarbonaceous residue. In this way the full quantity of carbon monoxide can be adsorbed.

When oxygen is preadsorbed and then ethene is passed over the catalysts, very little adsorption takes place and this can be interpreted in the same way as with a carbon monoxide precovered surface. However, when ethene is preadsorbed and then oxygen is passed over the samples, two completely different effects are observed. When this experiment is performed with the nitrate- or oxide-derived catalysts oxygen is adsorbed and carbon dioxide is produced; when the chloride-derived catalyst was used some oxygen was adsorbed but no carbon dioxide was formed. On passing the oxygen over the precovered nitrate- or oxide-derived catalysts reaction occurs giving rise to carbon dioxide. We cannot say whether any of the oxygen was adsorbed prior to reaction or whether the initial reaction is through gas-phase oxygen; however, immaterial of the reaction pathway, a considerable amount of carbon dioxide is produced and much more than the amount of ethene that was preadsorbed. The formation of this "excess" carbon dioxide, i.e., production of carbon dioxide greater than twice the amount of preadsorbed ethene, lends credence to the view that the hydrocarbonaceous deposit can polymerise or be built up during successive chemisorptions. With the chloride-derived catalyst the behaviour observed is fundamentally different: the fact that some oxygen can adsorb on the catalyst suggests that either the hydrocarbonaceous deposit is not reactive or that the adsorbed oxygen cannot come into close enough proximity with the deposit to initiate reaction. Why there should be this difference between the catalysts is not clear. The possibility of residual chloride affecting the reactivity of either the oxygen or hydrocarbon cannot be excluded even though we have been unable to detect any residual chloride. A second possibility may be that changes in particle size may alter the adsorption site: note that the most highly dispersed catalysts, the oxide- and nitrate-derived, do not adsorb ethene in the conventional random two-site mechanism, suggesting that the dispersion, especially when very high, may have a role in determining the mode of adsorption/reactivity of adsorbed species.

Although the adsorption of ethyne has been extensively studied (*11*), this is not the case with propyne. The total amounts of propyne adsorbed by the catalysts are similar to the amounts of ethene adsorbed, and this is similar to the behaviour observed with ethyne adsorption (*5*). However, the specific behaviour is considerably different from that observed with ethene or ethyne. All three catalysts behaved in slightly different ways on initial adsorption of propyne. The simplest was the adsorption on the chloride-derived catalyst: on this sample the behaviour mirrored that of ethene. The maximum uptake was observed on the first pulse and only a small amount of self-hydrogenation was noted; however, the product of the hydrogenation was not propane, as would have been expected if the system had mirrored the behaviour of ethyne adsorption, when ethane was the sole product (*5*). The production of the half-hydrogenated product is in keeping with results of propyne hydrogenation over pumice-supported rhodium (*12*), where a selectivity of 93% towards propene was observed. A similar result was obtained for propa-1,2-diene hydrogenation (*13*) where again propene is formed initially with a selectivity of ~95%. What is clear is that in a system where there is no preadsorbed hydrogen, very little self-hydrogenation occurs. When propyne was adsorbed on a nitrate-derived catalyst there was considerably more hydrogenation, with propene again being the hydrogenation product. The depressed adsorption over the first few pulses and the increased amount of hydrogenation suggest that there is hydrogen associated with the catalyst, so that even with excess hydrogen available the hydrogenation gives results in keeping with the propyne and propa-1,2-diene studies (*12, 13*). When propyne was adsorbed on a freshly reduced rhodium oxide/silica catalyst both methane and propene are formed, but no C-2 hydrocarbons. The production of methane was totally unexpected and is indicative of a hydrogenolysis reaction. It is interesting to note that even with a considerable excess of hydrogen present propene is still the hydrogenation product, even though hydrogenolysis is occurring.

On thermal desorption very little of the adsorbed propyne is desorbed in any form. This is similar to the behaviour observed with ethyne (*5*) where there is also considerable retention. Again we would suggest that the retained species polymerise in a manner similar to that proposed for ethyne (*14*), hence freeing part of the surface for subsequent adsorptions.

When the steady-state catalysts were precovered with propyne and carbon monoxide was adsorbed no gas was desorbed and only a fraction of the steady-state value was adsorbed: similar behaviour was observed with carbon monoxide preadsorption followed by propyne adsorption. This type of behaviour can be explained by having sites on which only carbon monoxide can adsorb, sites on which only propyne can adsorb, and sites on which they can both adsorb. This view is supported by the fact that the sum of propyne plus carbon monoxide adsorption is the same as carbon monoxide plus propyne, i.e., $21.19 \pm 1.89\ \mu\text{mol}\ (\text{g} \cdot \text{catalyst})^{-1}$.

When oxygen is adsorbed on a propyne precovered surface, although some oxygen was adsorbed with all the catalysts, no carbon dioxide was formed. This is an identical result to that found with the ethene–oxygen adsorptions over the chloride-derived catalyst. In that case we suggested that either the deposit was unreactive or the oxygen could not achieve close enough proximity to the hydrocarbon to react; as all three catalysts show no reactivity it would appear more likely, in this case, that the hydrocarbon is unreactive.

CONCLUSIONS

We have shown that three catalysts differing only in the metal salt used to prepare them have fundamentally different characteristics in (i) amount of hydrogen retained after reduction, (ii) adsorptive capacity for ethene and propyne adsorption, (iii) thermal desorption, and (iv) reactivity of the retained hydrocarbon. Why such major effects should be observed on changing the starting metal salt is not clear at present, but we hope in the near future to be able to further our understanding of this interesting behaviour.

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