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Infrared Spectra of 1,3-Butadiene Adsorbed on Alumina-supported Metal Catalysts at Various Temperatures

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The infrared spectra of 1,3-butadiene adsorbed on Pd, Ni, and Co catalysts were measured while changing the adsorption temperature. These catalysts behaved differently in butadiene adsorption, and π-adsorbed butadiene was the major adsorbed species below 0 °C on Pd and Ni. This π-species was easily hydrogenated to produce butene at the same temperature.

There have been many infrared spectroscopic studies of hydrocarbons, especially olefins, adsorbed on transition metals.[1–3] The spectra of chemisorbed olefins have been measured mostly using supported metals at room temperature, and have been demonstrated to be of a complex nature caused by the existence of various dissociatively adsorbed hydrocarbons on the metal surface. Although π-bonded olefins on metal catalysts have been considered to be the intermediates of such reactions as hydrogenation, there has been no definite evidence from infrared spectroscopic measurements of the species on the metal surface. Recently π-adsorbed ethylene on Pd was observed from the difference in the spectra of the adsorbed species before and after hydrogenation[4] or in a low-temperature measurement.[5]

The hydrogenation reaction of 1,3-butadiene on transition metals has been studied in detail by Bond, Wells, and their co-workers.[6] According to their investigations, the reaction rate is proportional to the first order of the hydrogen pressure, while it is nearly proportional to the zero order of the butadiene pressure, like other olefin hydrogenation reactions. The composition of hydrogenated products (1-butene, *trans*- and *cis*-2-butene) varies depending on the metals and on the method of preparing the catalysts; this suggests the importance of the configurations of the adsorbed butadienes on the surface in deciding the compositions of hydrogenated products, kinds of butene. They considered three types of adsorbed butadiene: mono-π-bonded species, and *trans*- and *cis*-di-π-bonded species. Therefore, the direct measurement of the infrared spectra of adsorbed species will be helpful in understanding the mechanism and selectivity of the reaction.

The infrared spectra of butadiene adsorbed on Ni at room temperature were investigated by Erkelens,[3] and only methylene-rich polymeric species were observed. On Pd metal, no absorption band for adsorbed species appeared at room temperature, but that of polymerized species was observed after hydrogen addition.[2]

In this paper the infrared spectra of butadiene adsorbed on alumina-supported Ni, Pd, and Co catalysts will be reported in the temperature range between room temperature and −80 °C. At low temperatures, the side reactions were supressed and the spectra of π-bonded butadiene were clearly observed. The differences between the three metal catalysts in the adsorption of 1,3-butadiene were demonstrated to be of interest in connection with their catalytic properties in the hydrogenation reaction.

Experimental

Nickel or cobalt catalyst was prepared from a suspension of alumina in an aqueous solution of each metal nitrate, which was decomposed in air at 450 °C. Palladium particles were deposited on alumina in a $PdCl_2$ solution with the addition of formaldehyde and sodium hydroxide. Each of these catalysts contains about 9 wt % metal.

These catalysts were used in the shape of discs for the infrared measurements. For room-temperature measurements, the disc was evacuated at 420 °C for 2 h in an infrared cell and then reduced in hydrogen for 3 h at the same temperature. About 60 Torr of gaseous butadiene was placed in contact with the Ni catalyst for 15 min, but with Co catalyst for 20 h, and the spectra were measured after the cell was evacuated to 10^{-3} Torr. The cryogenic cell for low-temperature measurements was similar to that used by Avery.[2] As the highest temperature which could be attained with this cell was about 300 °C, the disc was evacuated and reduced at 400 °C in an glass vessel; the disc was then transferred to the cryogenic cell and was reduced again at 300 °C. The catalyst was placed in contact with gaseous butadiene for about 30 min; the butadiene was then removed by trapping and evacuation to 10^{-3} Torr. The adsorption of butadiene on an alumina support is negligible under these experimental conditions.

The 1,3-butadiene(*h*-butadiene) (Tokyo-Kasei Co.) and 1, 3-butadiene-1,1,4,4-d_4(CD_2=CH–CH=CD_2) (MSD Co.) were purified by passing it through a heated palladium thimble.

Gas chromatography with a DMF-alumina column was used for the analysis of gaseous hydrocarbons.

Results

Palladium. Figure 1 shows a spectrum of $\Delta^{1,3}$-C_4H_6 chemisorbed on Pd-Al_2O_3 at −32 °C, together with the band frequencies of Fe–butadiene complexes and free butadiene. It is evident that the spectrum is quite different from that of gaseous butadiene, but corresponds to that of Fe–butadiene complexes except for a broad band at 1653 cm^{-1}. The assignment of the bands of chemisorbed $\Delta^{1,3}$-C_4H_6 can be made on the basis of the results for the Fe–C_4H_6 complex reported by Davidson *et al*:[7] 1433 for $\nu_{C=C}$, 1224 cm^{-1} for ν_{C-C}, and 1473 and 1376 cm^{-1} for CH_2 scissors vibrations. (π_d)* The existence of the band at 1653 cm^{-1} shows that a part of the chemisorbed butadiene has a

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* π_s and π_d show two adsorbed species of butadiene on Pd below 0 °C. These structures will be shown in the 'Discussion' section.

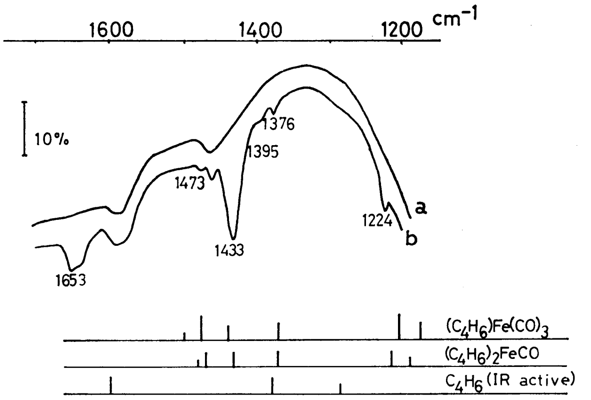


Fig. 1. IR spectrum of $\Delta^{1,3}$-C_4H_6 adsorbed on Pd-Al_2O_3 at −32°C(b), (a) Pd-Al_2O_3 background. The lines under the spectra show the positions and band intensities of Fe-C_4H_6 complexes and gaseous C_4H_6.

free C=C double bond and has another C=C bond interacting with the surface Pd. (π_s)*

The existence of two kinds of adsorbed species (π_d, π_s) is consistent with the fact that the band intensity at 1653 cm^{-1} relative to that at 1433 cm^{-1} varies with the butadiene coverage and the temperature. The ratio of these peak intensities was about 0.34 when a small amount of butadiene was adsorbed at −80 °C, while the value reached 0.60 when adsorption was saturated at −25 °C. If it is assumed that the band at 1433 cm^{-1} is due to both π_s and π_d species, while the band at 1653 cm^{-1} is due only to the π_s species, the relative amount of the π_s species can be estimated to be small at a low butadiene coverage, but to increase with a rise in the adsorption temperature. The rate of the decrease of the absorbance at 1653 cm^{-1} upon D_2 addition is 1.2 times faster than that of the absorbance at 1433 cm^{-1} on both Pd and Ni at −50 °C. These observations indicate that the π_s species is less stable than the π_d species.

When hydrogen was introduced on butadiene chemisorbed over a Pd catalyst at −50 °C, new bands attributable to the formation of a methyl group and a co-ordinated C=C double bond appeared, as is shown in Fig. 2. These bands which appeared upon hydrogen addition (indicated by arrows in Fig. 2c) are closely related to the bands of butene in K[$PtCl_3$(*trans*-C_4H_8)],[9] except for a part of the band at 1650 cm^{-1} which disappeared easily upon evacuation and the band at 1580 cm^{-1}. The only gaseous products were butenes and *n*-butane, and the butenes adsorbed on Al_2O_3 showed a band at 1580 cm^{-1}, so the above two bands may be attributed to gaseous butene and to butene adsorbed on Al_2O_3 respectively. It may be concluded that the π-species of chemisorbed butadiene was hydrogenated to form chemisorbed butene, a part of which was liberated into the gas phase or adsorbed on Al_2O_3.

At room temperature, no spectrum of butadiene adsorbed on Pd was observed, in agreement with the result by Avery,[2] whereas weak bands due to the formation of a methyl group were observed after hydrogen addition.

Nickel. The spectrum of $\Delta^{1,3}$-C_4H_6 chemisorbed on Ni at low temperatures (−78—0 °C) is almost identical to that chemisorbed on Pd. The spectrum changed, however, as is shown in Fig. 3, when the temperature was raised, and new bands appeared which could not be removed by room-temperature evacuation. The spectra at room temperature are shown in Fig. 4, while the observed frequencies and their assignments are listed in Table 1. The two adsorbed species can be distinguished from each other on the basis of their behavior

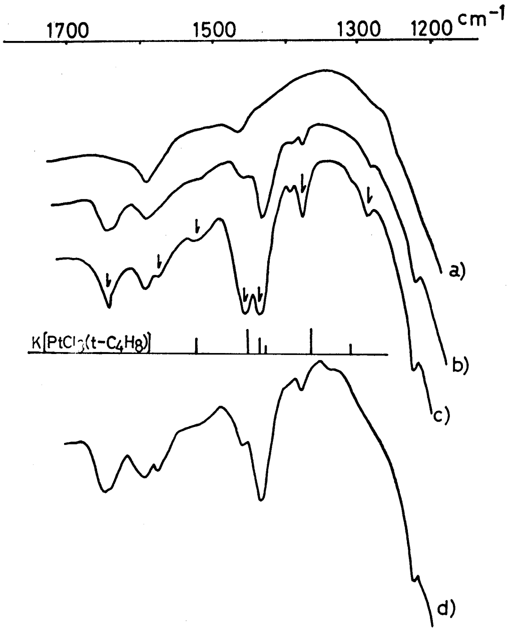


Fig. 2. IR spectra of $\Delta^{1,3}$-C_4H_6 adsorbed on Pd-Al_2O_3 at −50°C and spectral changes with addition of H_2. a) Background. b) Chemisorbed $\Delta^{1,3}$-C_4H_6 at −50°C. c) After introduction of 25 Torr H_2. Arrows show the bands which appeared by H_2 addition. d) Evacuated to 10^{-3} Torr. The inserted lines show the band positions and strengths of Pt-C_4H_8 complex.

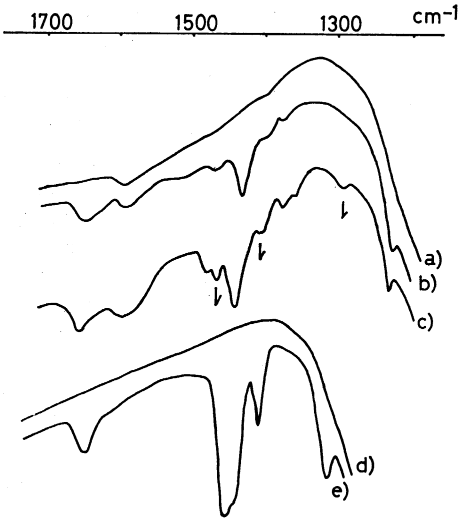


Fig. 3. IR spectra of $\Delta^{1,3}$-C_4H_6 adsorbed on Ni-Al_2O_3 at various temperatures.
a) Background of the spectra b and c. b) −35°C. c) 15°C. d) Background of the spectrum e. e) Room temperature. Arrows show the bands increased in intensity at higher temperatures.

upon hydrogen addition; the intensity of one increases, while that of the other decreases. The former bands can be assigned to the CH_2 stretching (2925, 2854) and CH_2 scissors (1467 cm^{-1}) of polyethylene. The latter bands are located at 3010, 1650, 1440, 1407, and 1308 cm^{-1} and may be assigned as is shown in Table 1. The weak band at 1370 cm^{-1} and the shoulder at about 2960 cm^{-1} may be due to the methyl group. In the case of butadiene-d_4, the bands at 3006, 2955, 2300, 2125, 1645, and 1403 cm^{-1} decreased in intensity upon hydrogen addition.

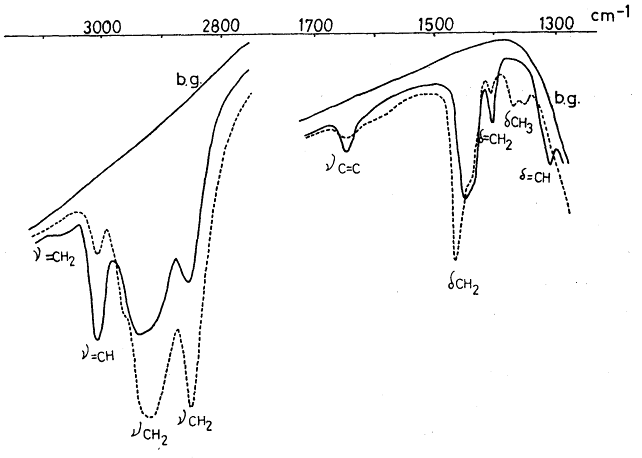


Fig. 4. IR spectrum of $\Delta^{1,3}$-C_4H_6 adsorbed on Ni-Al_2O_3 at room temperature(——) and that after hydrogen was introduced (----). b. g.; Ni-Al_2O_3 background.

Table 1. Observed frequencies of 1,3-butadiene chemisorbed on Ni-Al_2O_3 at room temperature, the intensity changes of these bands upon hydrogen addition, and the band assignments

CH_2=CH-CH=CH_2 cm^{-1}	New bands appearing after H_2 addition cm^{-1}	Intensity changes after H_2 addition	Assignments
3075		decreased	$\nu_{=CH_2}$
3010		decreased	$\nu_{=CH}$
	2960 sh		ν_{CH_3}
2925		increased	ν_{CH_2}
2854		increased	ν_{CH_2}
1650		decreased	$\nu_{C=C\ free}$
	1467		δ_{CH_2}
1440		decreased	$\delta_{=CH_2}$ or $\nu_{C=C\ ads.}$
1407		decreased	$\delta_{=CH}$
	1370		δ_{CH_3}
1308		decreased	$\delta_{=CH_2}$

CD_2=CH-CH=CD_2 cm^{-1}	New bands appearing after D_2 addition cm^{-1}	Intensity changes after D_2 addition	Assignments
3006		decreased	$\nu_{=CH}$
2955		decreased	ν_{-CHM-}
2910		increased and shifted to 2897cm^{-1}	ν_{CH}
	2860 sh		
2300		decreased	$\nu_{=CD_2}$
2210		increased and shifted to 2202 cm^{-1}	ν_{CD_2}
2125		decreased	ν_{-CD_2M}
2100		increased and shifted to 2106 cm^{-1}	ν_{CD_2}
1645		decreased	$\nu_{C=C\ free}$
1403		decreased	$\delta_{=CH}$
	1308		δ_{CHD}

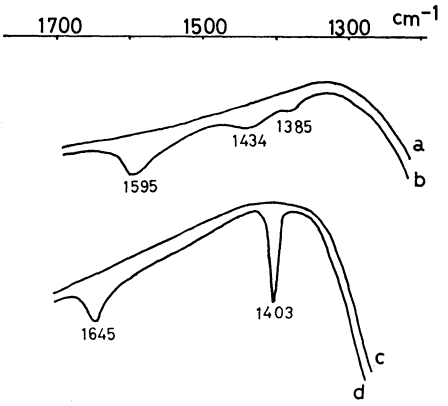


Fig. 5. IR spectra of CD_2=CH-CH=CD_2 adsorbed on Ni-Al_2O_3.
a, c) Background. b) Adsorption at −29°C. d) Adsorption at room temperature.

The adsorbed species, the amount of which decreased upon hydrogen addition at room temperature, can be considered to be different from those (π_d, π_s) observed below 0 °C, because the former species shows sharp bands at 1407 and 1308 cm^{-1} which were not observed in the π_d and π_s species of *h*-butadiene. Furthermore, the spectra of butadiene-d_4 changed remarkably with a change in the adsorption temperature, as is shown in Fig. 5. The free C=C double bond stretching band was observed at 1595 and 1645 cm^{-1} in low-temperature and room-temperature spectra respectively. This fact supports the above-mentioned deduction, since the adsorption of butadiene-d_4 produces, probably, the same species as *h*-butadiene adsorption.

The rate of butadiene hydrogenation to butene was zero-order to the butadiene pressure, and proportional to the hydrogen pressure, on the Pd and Ni catalysts in the low-temperature range (−60—10 °C) and on Co between 0 and 100 °C. The number of active sites of butadiene hydrogenation can be estimated from the amount of the C_4 species (C_4H_8+C_4H_{10}) formed by the addition of hydrogen to chemisorbed butadiene. As is shown in Table 2, the amount of C_4 species desorbed from the Ni catalyst by hydrogen decreases with an increase in the adsorption temperature, though the amount of butadiene adsorbed has a tendency to increase because of polymerization on the surface. At −31.5 °C almost all of the Ni atoms on the surface are active in hydrogenation, but at higher temperatures, polymerization on the surface destroys the active sites

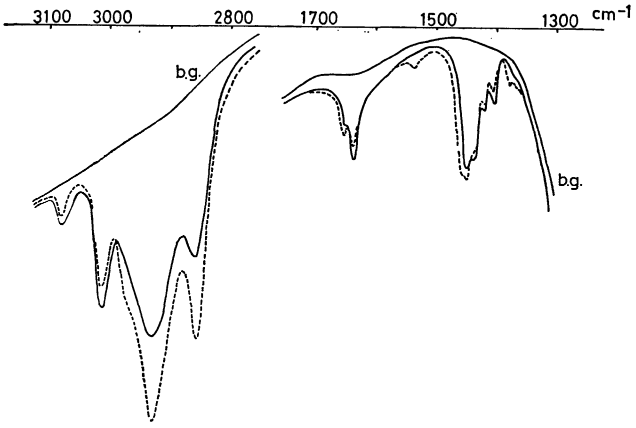


Fig. 6. IR spectrum of $\Delta^{1,3}$-C_4H_6 adsorbed on Co–Al_2O_3 at room temperature(——) and that after hydrogen was introduced(-----). b. g.; Co–Al_2O_3 background.

for hydrogenation to butene. The number of active sites at room temperature is less than 10% of the surface Ni atoms.

Cobalt. Figure 6 shows the spectrum of butadiene chemisorbed on Co–Al_2O_3 at room temperature and that after hydrogen addition. The adsorption at room temperature was very slow, and the catalyst had to be in contact with butadiene for 20 h to obtain a sufficient intensity of the spectrum of the adsorbed species. When butadiene was in contact for 20 h, several weak bands appeared at 2960, 2920, 2860, 1460, and 1370 cm^{-1} on Al_2O_3 without metal. Though the spectra of chemisorbed species on Co–Al_2O_3 resemble, as a whole, those on Ni at room-temperature adsorption, some significant differences can be noted. The difference between Ni and Co spectra can be clearly seen in Fig. 7.

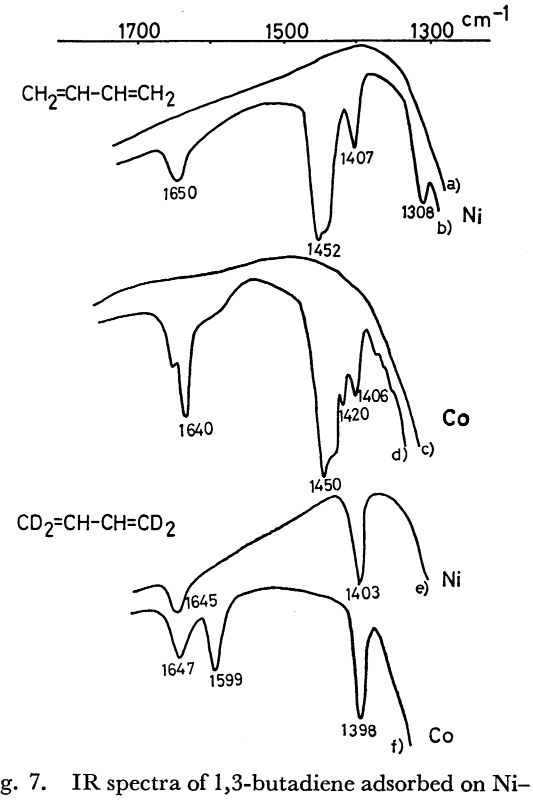
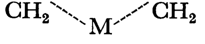


Fig. 7. IR spectra of 1,3-butadiene adsorbed on Ni– and Co–Al_2O_3 at room temperature.
a, c) Background. b, d) C_4H_6 adsorption on Ni and Co resp. e, f) $C_4H_2D_4$ adsorption on Ni and Co resp.

Discussion

Palladium. When pre-adsorbed butadiene on Pd was removed by introducing hydrogen below 0 °C, the gaseous products were butadiene, butene, and butane. Thus, butadiene may be considered to be non-dissociatively adsorbed on Pd in this temperature range. The observed similarity between the spectrum of butadiene chemisorbed on the Pd surface and that of the Fe complex may indicate that one type of adsorbed butadiene on Pd has the following structure, as butadiene in the Fe complex has a *cis* configuration with the two C=C bonds π-bonded to Fe:[7]

π_d;



It may be considered there exists another species which has a free C=C stretching band at 1653 cm^{-1}. The only band which were distinct to this species was the band at 1653 cm^{-1}, so it is reasonable to consider this species to have a structure similar to that of the above species, π_d. Thus, the following structure may be considered:

$$\pi_s;\quad CH_2{=}CH{-}\underset{\underset{M}{|}}{CH}{=}CH_2$$

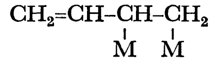
It has been reported that the butadiene in the $[PdCl_2(C_4H_6)]_2$ complex is monodentate at −40 °C and that it gives the free C=C stretching band at 1660 cm^{-1} and a strong band around 1440 cm^{-1}.[8] Because the C=C stretching band is presumed to exhibit the largest shift with the change in the nature of π-bonding between butadiene and a metal atom, it is not unreasonable that the remaining bands of this π_s butadiene could not be observed from π_d butadiene.

Nickel. Butadiene chemisorbed on Ni below 0 °C must have structures similar to those chemisorbed on Pd, judging from the agreement of the spectrum; those were π_s and π_d.

However, the spectrum at room temperature is different from that below 0 °C. The former spectrum is explained as showing the co-existence of two adsorbed species; one is polyethylene, whose intensity increased upon hydrogen addition:

$$\text{polymer: } -(CH_2)_n-$$

From the spectra it was deduced that the other species had C=C, CH_2=, and CH= groups in *h*-butadiene and C=C, CD_2=, =CH, –CHM–, and –CD_2M groups in butadiene-d_4. Although the stretching bands due to –CHM– and –CH_2M groups in *h*-butadiene could not be observed, those bands were considered to overlap with the strong bands of polyethylene. The species with these bands most probably has the structure:



$$\sigma:\ CH_2{=}CH{-}\underset{\underset{M}{|}}{CH}{-}\underset{\underset{M}{|}}{CH_2}$$

Cobalt. There are one σ-type species and one polymeric species on Ni, whereas on Co there is still another adsorbed species which decreased in intensity upon hydrogen addition at room temperature, as is shown in Fig. 7. The third species has the bands at 1640 and 1420 cm^{-1} for C_4H_6 and at 1599 cm^{-1} for butadiene-d_4. As the bands of the species on Co agree with those on Pd or Ni in the low-temperature range, and are assigned to π-adsorbed species (π_s, π_d), the two kinds of π-adsorbed species remain stable at room temperature on Co, though they are unstable on Pd and Ni.

The observed species of 1,3-butadiene chemisorbed on alumina-suported Pd, Ni, and Co catalysts can be summarized as follows:

	Low temperatures (−50—0 °C)	Room temperature
Pd	$\pi_s+\pi_d$	—
Ni	$\pi_s+\pi_d$	polymer$+\sigma$
Co	—	polymer$+\sigma+\pi_s+\pi_d$

The σ-type species was easily hydrogenated at room temperature and can be considered to be a precursor of polyethylene and/or 1-butene.

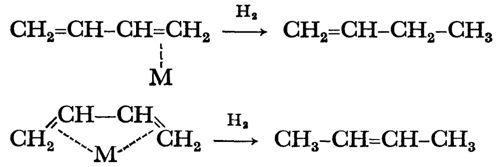
The π-species which were observed on Pd and Ni at low temperatures and on Co at room temperature were composed of two species (π_s, π_d), and the π_s species was less stable than the π_d species. These π-adsorbed species covered almost all of the Ni surface atoms at low temperatures (−35 °C), as is shown in Table 2, and were easily hydrogenated by hydrogen to form adsorbed butene at the same temperature (Fig. 2).

TABLE 2. DESORPTION PRODUCTS OF ADSORBED C_4H_6 ON Ni–Al_2O_3, WHICH WERE REMOVED BY THE ADDITION OF H_2[a)]

T °C	Amounts of desorbed species ($C_4H_3+C_4H_{10}$) mol/g-cat	(C_4H_6)	Amounts of surface Ni atoms[b)] mol/g-cat
−31.5	8.37×10^{-5}	0.77×10^{-5}	9.78×10^{-5}
2	3.69	0.62	
29.8	0.71	0.54	

a) 75 Torr of C_4H_6 was adsorbed for 30 min at the above temperature and evacuated to 0.03 Torr, and then 25 Torr of hydrogen was introduced to hydrogenise and remove the adsorbed species. The gaseous desorption products were C_4H_6, C_4H_8, and C_4H_{10}. b) The Ni surface area was estimated from the amount of H_2 adsorbed at 0 °C.

The π_s species may be considered to be a precursor of 1-butene, and the π_d species, to be that of 2-butene in butadiene hydrogenation.



$$\underset{\overset{\vdots}{M}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{H_2} CH_2{=}CH{-}CH_2{-}CH_3$$

π-Bonded ethylene was observed by IR measurement on Al_2O_3-supported Pd or Pt catalysts at low temperatures (−86 °C) as the main adsorbed species on the surface,[5)] whereas the main adsorbed species were σ-bonded or dissociatively adsorbed species at room temperature.[1,4)] In the butadiene adsorption, also σ-type and polymerized species were shown to be formed on Ni only above room temperature, while π-bonded species were observed at low temperatures. These facts indicate that π-bonded species of olefins which are considered to be precursors of hydrogenation reaction, become predominant on transition metals at low temperatures, where the reactivity of the metal catalysts is lowered. It is interesting that Pd, Ni, and Co behave differently from each other in butadiene adsorption; the difference in the stability of π-adsorbed species on Pd and Ni from that on Co, and the existence of polymerized species on Ni and Co, which decreases the active sites for hydrogenation reaction.

Wells and his co-workers discriminate various Ni or Co catalysts as Type A or Type B for butadiene hydrogenation.[6)] According to them, the 1,2-addition of hydrogen is preferred on a Type A catalyst, while on a Type B catalyst 1,4-addition occurs mainly. All the catalysts used here (Ni, Co, and Pd) showed Type A behavior; more than 50% of the butene produced was 1-butene, although the *trans*: *cis* ratio was high on Pd (7—8), but low on Ni and Co, (2—3). Type B behavior could not be observed even when the reduction temperature was raised above 400 °C; this might be because of the small metal particle size of these catalysts (less than 60 Å).

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References

1) B. A. Morrow and N. Sheppard, *Proc. R. Soc. London, Ser. A*, **311**, 391, 415 (1969); A. Ravi and N. Sheppard, *J. Phys. Chem.*, **76**, 2699 (1972); G. Blyholder and W. V. Wyatt, *J. Phys. Chrm.*, **78**, 618 (1974).

2) N. R. Avery, *J. Catal.*, **19**, 15 (1970).

3) J. Erkelens, *J. Catal.*, **37**, 332 (1975).

4) J. D. Prentice, A. Lesiunas, and N. Sheppard, *J. Chem. Soc. Chem. Commun.*, **1976**, 76.

5) Y. Soma, *J. Chem. Soc. Chem. Commun.*, **1976**, 1004.

6) G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Chem. Soc.*, **1965**, 3218; J. J. Phillipson, P. B. Wells, and G. R. Wilson, *J. Chem. Soc., A*, **1969**, 1351; A. J. Bates, Z. K. Leszczyński, J. J. Phillipson, P. B. Wells, and G. R. Wilson, *ibid.*, **1970**, 2435; R. G. Oliver and P. B. Wells, "Proceedings of the 5th International Congress on Catalysis, 1972," North-Holland Publishing Co., Amsterdam (1973), Paper 44, p. 659.

7) G. Davidson and D. A. Duce, *J. Organomet. Chem.*, **44**, 365 (1972).

8) M. Donati and F. Conti, *Tetrahedron Lett.*, **1966**, 1219.

9) J. Hiraishi, D. Finseth, and F. A. Miller, *Spectrochim. Acta, Part A*, **25**, 1657 (1969).