Sampling Catalysis Research in the Pannonian Region

Proceedings of the 8th Pannonian International Catalysis Symposium

Supported by

International
Visegrad Fund
www.visegradfund.org

Jointly organised by

The Hungarian Zeolite Association
and
The Catalysis Club of the Hungarian Academy of Sciences

2006
Szeged, Hungary

Symposium Committee

Miroslav Derewinski, Poland
Hannelore Vinek, Austria
Milan Hronec, Slovak Republic
Árpád Molnár and Imre Kiricsi, Hungary
Zdenek Sobalík, Czech Republic

Organising Committee

Árpád Molnár (Chairman) and
Imre Kiricsi (Co-Chairman)
Attila Wootsch and Sándor Gőbölös (Secretaries)
István Pálinkó (Treasurer)
Klára Hernádi, János Halász, István Hannus,
Ákos Kukovecz, Zoltán Kónya, Mónika Urbán

Technical editor: István Pálinkó

ISBN 963 06 0138 9

Published by the Hungarian Zeolite Association

The formation of carbonaceous layer from ethylene over various transition metal catalysts – an FT-IR study

*Bálint Szilágyi, János T. Kiss, István Pálinkó**

Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720
Hungary

Abstract

The ethylene-derived carbonaceous overlayers were studied over silica-supported Pt, Pd, Rh and Cu catalysts by FT-IR spectroscopy under desorption conditions. As a general feature it was observed over all catalysts that upon increasing the desorption temperature the overlayer gradually became poor in hydrogen. The structure of the overlayers was similar over the silica-supported Pt, Pd and Rh. On increasing the reaction temperature the σ-adsorbed half-hydrogenated species are transformed to adsorbed ethylidyne. On the Cu catalyst prepared with ion exchange a similar picture emerged, while on those prepared with precipitation ethylidyne soon became the predominant species. Hydrogen swept off the carbonaceous species from the transition metals, however, copper retained large portions of it.

1. Introduction

In most metal-catalysed hydrocarbon reactions the originally clean metal surface soon becomes covered with carbonaceous residues of varying hydrogen content [1]. Depending on various factors but mainly on reaction temperature the carbonaceous layer can be rich in hydrogen influencing the surface reactions as reactive part of the catalytic system or can act a catalyst poison as its hydrogen content is diminished and the carbonaceous layer turns more and more graphitic [2]. Beside reaction temperature the nature of the metal should play important role, one rightly expects differences in these carbonaceous layers as one moves from noble metals (Pt, Pd, Rh) to an early transition metal as Cu. In this contribution this kind of account is given. The carbonaceous layer was built from the chemisorption of ethylene over silica-supported Pt, Pd, Rh or Cu, and the behaviour of the layer on temperature treatment was investigated by FT-IR spectroscopy.

2. Experimental

The silica-supported Pt, Pd and Rh catalysts were prepared by impregnation followed by high temperature reduction in flowing hydrogen. Various silica-supported Cu catalysts were made either by precipitation or ion exchange followed by stepwise reduction in hydrogen. Characteristic data on the catalysts are given in Table 1.

Catalyst samples were treated with small amounts of ethylene (1 kPa) in a vacuum system at somewhat higher temperature (353 K) than usual to facilitate chemisorption. The chemisorbed layer was studied by IR spectroscopy, just as the layers obtained after a stepwise increase in catalyst temperature (353–573 K temperature range) followed by evacuation. The CH stretching, the deformation as well as the overtone regions were investigated. It is to be noted that hydrogen was not added to the hydrocarbon either before or during chemisorption and heat treatments. In separate experiments hydrogen (1 kPa) was added during desorption.

Table 1
Characterising data on the catalysts

Metal	Support	Loading (%)	Dispersion (%)	Method of preparation
Pt	Cab-O-Sil	3	11.8	Impregnation
Pd	Cab-O-Sil	3.0	15.4	Impregnation
Rh	Cab-O-Sil	3.2	27.0	Impregnation
Cu	Cab-O-Sil	6.8	9.5	Precipitated
Cu	Cab-O-Sil	3.91	11.9	Ion exchange
Cu	Silica	6.36	14.3	Ion exchange
Cu	Silica	1.91	16.9	Ion exchange

For IR measurements were performed with a Bio-Rad FTS-65A/896 spectrometer equipped with a DGTS detector. Resolution was 4 cm-1 and 128 scans were collected for a spectrum. Spectra were baseline-corrected and those of water vapour were subtracted. The catalysts were pressed to self-supported wafers and spectra were detected under desorption conditions. Species were identified as follows:

(i) 3070 cm^{-1} (ν_{as}=CH_2), 3020 cm^{-1} (ν=CH), 2995 cm^{-1} (ν_s=CH_2), 1425 cm^{-1} (δ=CH_2) – π-adsorbed complex [3]

(ii) 3020 cm^{-1} (ν=CH), 1500 cm^{-1} (νC=$C/\delta CH_2$), 1200 cm^{-1} ($\delta CH_2/\nu C$=C) – $\pi\sigma$-adsorbed complex

(iii) 2910 cm^{-1}, 1420 cm^{-1} – σ-diadsorbed complex [3, 4]

(iv) 2880 cm^{-1} ($\nu_s CH_3$), 1340 cm^{-1} ($\delta_s CH_3$)1130 cm^{-1}, 1115 cm^{-1}, 1090 cm^{-1}, 1155 cm^{-1}, 1130 cm^{-1} (all νCC vibrations) – ethylidyne adsorbed complex [5]

3. Results and Discussion

3.1. The ethylene–supported metal systems without added hydrogen

The behaviour of the silica-supported Pt, Pd and Rh catalysts was found to be similar, thus observations concerning the ethylene–Pt/Cab-O-Sil system (Fig. 1) are only detailed below.

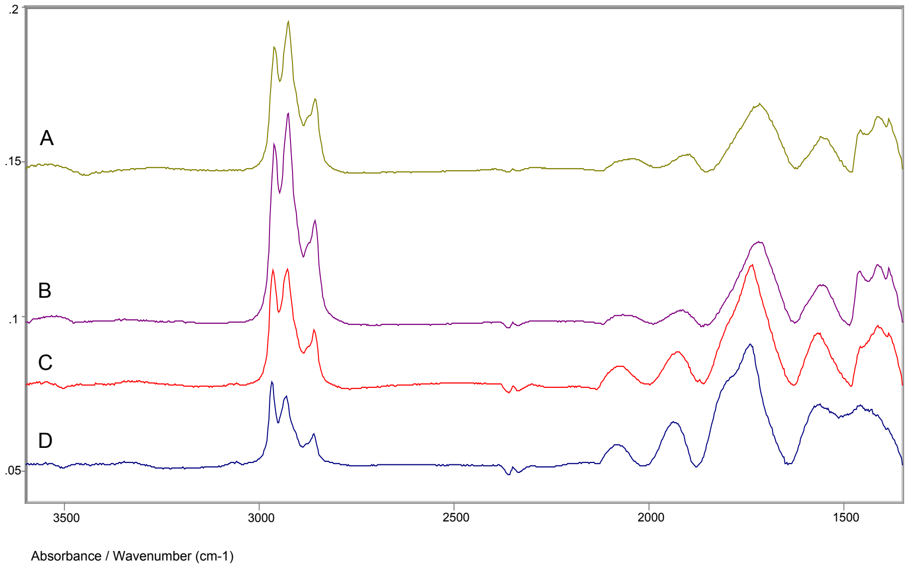

Fig.1. The FT-IR spectra of the ethylene–Pt/Cab-O-Sil system under desorption conditions. Adsorption of 1 kPa ethylene at 353 K, followed by 10 min evacuation at (A) 298 K, (B) 353 K, 473 K, (D) 573 K.

The two bands appearing at the highest wavenumbers may be attributed to the $\nu_{as}CH_3$ and $\nu_{as}CH_2$ vibrations, while the poorly decomposed signal at 2860 cm^{-1} are symmetric counterparts. These bands may be assigned to the half-hydrogenated state, i.e. the σ-bonded ethyl group.

The intensities of the bands at 2963, 2927 and 2858 cm^{-1} increase up to the 353 K desorption temperature, then they decrease. The decrease is significantly faster for the band at 2927 cm^{-1} than that of one at 2963 cm^{-1}. The increase in the desorption temperature does not influence the positions of these bands significantly, however, induces significant alterations in the bands detectable in the 2100-1700 cm^{-1} region.

The above-described results indicate that σ-adsorbed half-hydrogenated species predominate over the silica-supported Pt. Pd and Rh catalysts without added hydrogen at room temperature. On increasing the desorption temperature the ratio of the intensities of the CH_3 to CH_2 groups increases, i.e. ethylidyne species take over. Let us note already here that on the addition of hydrogen they instantly desorb in the form of ethylene.

Although the detected IR spectrum of the precipitated 6.8% Cu/Cab-O-Sil catalyst was similar to what was observed over the transition metal catalysts at the adsorption temperature, the increase in desorption temperature did not influence the intensity of the $\nu_{as}CH_3$ band (Fig. 2). This was the only copper catalyst displaying this phenomena. It is very probable that a stabile ethylidyne layer is formed on adsorption, which survives the increasing desorption temperature.

Over the ion-exchanged 3.9% Cu/Cab-O-Sil the most intense band was at 2963 cm^{-1}, however, its intensity decreased with increasing desorption temperature and at 473 K and above it shifted to 2970 cm^{-1} (Fig. 3). The intensities of band at 2928 and 2859 cm^{-1} also decreased. Parallel with the bands of the valence vibrations, those of the bond deformation region (2100 cm^{-1}–1700 cm^{-1}) also decreased substantially.

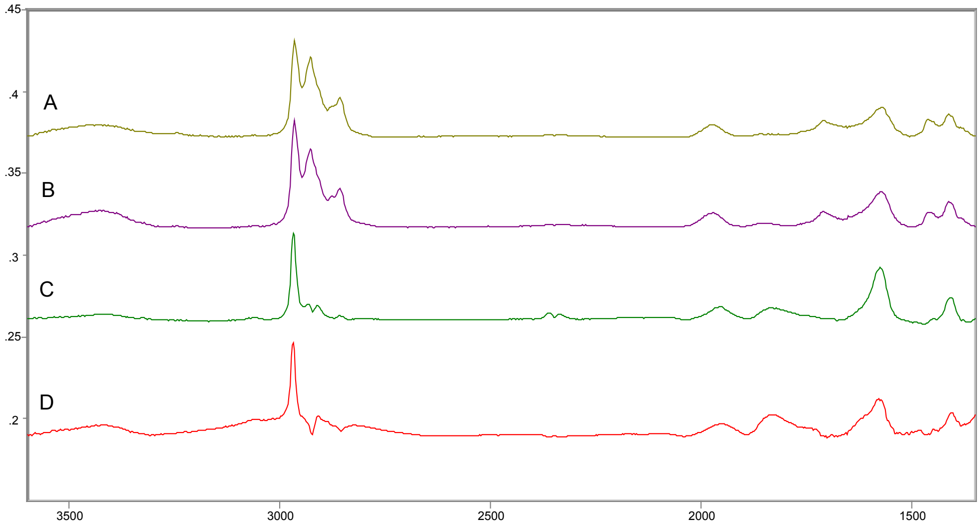

Fig. 2. The FT-IR spectra of the ethylene–6.8% Cu/Cab-O-Sil (prepared with precipitation) system under desorption conditions. Adsorption of 1 kPa ethylene at 353 K, followed by 10 min evacuation at (A) 298 K, (B) 353 K, (C) 473 K, (D) 553 K.

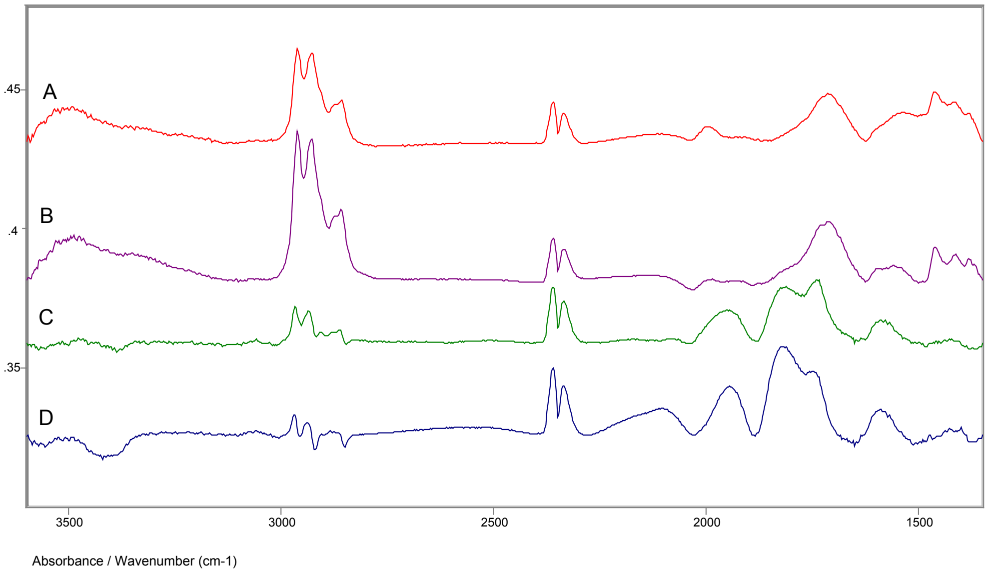

Fig. 3. The FT-IR spectra of the ethylene–3.91% Cu/Cab-O-Sil (prepared with ion exchange) system under desorption conditions. Adsorption of 1 kPa ethylene at 353 K, followed by 10 min evacuation at (A) 298 K, (B) 353 K, (C) 473 K, (D) 553 K.

Over the 6.36% ion-exchanged Cu/SiO_2 the most intense bands appeared at 2963, 2928 and 2858 cm^{-1}. The intensities of these bands increased up to 393 K, then decreased considerably with further raising the temperature. On increasing the temperature a small band appeared at 3065 cm^{-1} and started to grow gradually and to shift to 3058 cm^{-1}.

In the region of deformation vibrations bands appeared at 1460, 1416 and 1383 cm^{-1}. Their intensities grew up to 393 K, then, they decreased at higher temperatures. The band at 1416 cm^{-1} shifted to 1429 cm^{-1}.

The ion-exchanged 1.91% Cu/Cab-O-Sil catalyst behaved similarly to the previous copper catalyst.

Comparing the behaviour of the copper catalysts it is clear that their methods of preparation were decisive and not the loading. Catalysts prepared with the ion-exchange method displayed similarities with the silica-supported transition metals, except that ethylidyne species at high desorption temperatures were not so important. Over the copper catalyst prepared with precipitation, however, ethylidyne species were the most important from the beginning.

3.2. The ethylene–silica-supported copper systems with added hydrogen

Unlike the transition metal catalysts copper retains carbonaceous deposits even in the presence of hydrogen.

Over the 6.8% Cu/Cab-O-Sil catalyst prepared with precipitation the valence bond vibration region contained bands at 2963, 2926 and 2857 cm^{-1} (Fig. 4). Other important bands can also be identified in the deformation region (1700 cm^{-1} and 1450 cm^{-1}). Heat treatment only hardly influenced the positions of these bands. Hydrogenation did not fully remove hydrocarbonaceous deposits even at high temperature.

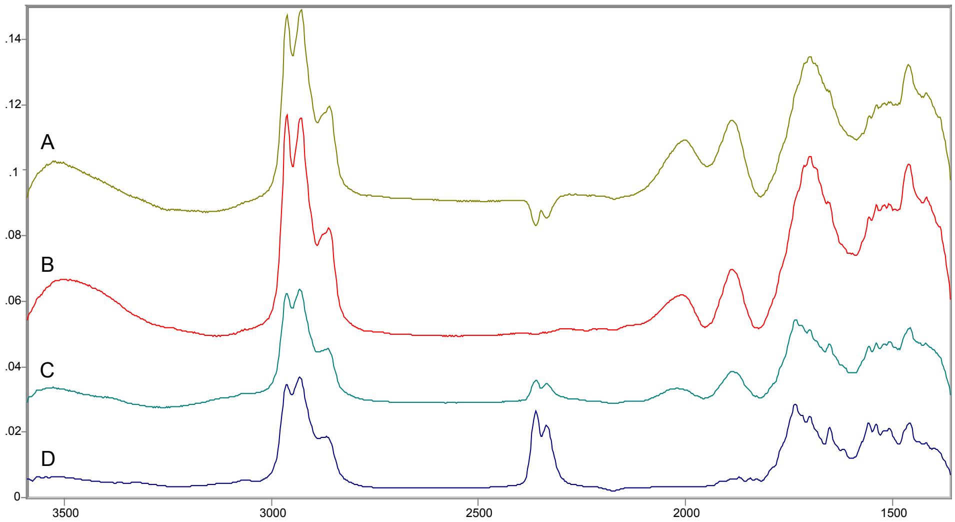

Fig. 4. The FT-IR spectra of the H_2–ethylene–6.8% Cu/Cab-O-Sil (prepared with precipitation) system. Adsorption of 1 kPa ethylene at 353 K, followed by 10 min evacuation at (A) 298 K. Adding 1 kPa of H_2 followed by 10 min evacuation at (B) 353 K, (C) 473 K, (D) 553 K.

Over the ion-exchanged 6.36% Cu/SiO$_2$ catalyst the positions and the behaviour of bands were different from the previous catalyst (Fig. 5). They also differed from those identified over this catalyst without added hydrogen. The band at 3210 cm^{-1} could be removed with hydrogenation already at 393 K. A new band at 3068 cm^{-1} appeared after adding hydrogen. Its intensity did not change up to 473 K, then, it increased on treatment at 553 K. The intensities of the bands at 2962, 2927 and 2861 cm^{-1} decreased on increasing temperature, however, the bands did not disappear even at the highest temperature applied.

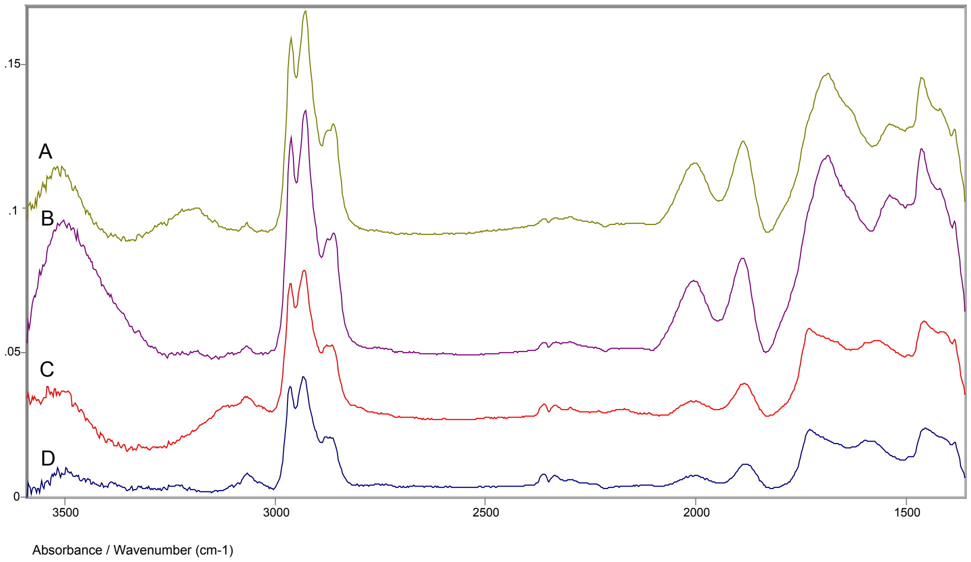

Fig. 5. The FT-IR spectra of the H_2–ethylene–6.36% Cu/SiO_2 (prepared with ion exchange) system. Adsorption of 1 kPa ethylene at 353 K, followed by 10 min evacuation at (A) 298 K. Adding 1 kPa of H_2 followed by 10 min evacuation at (B) 353 K, (C) 473 K, (D) 553 K.

4. Conclusions

FT-IR spectroscopy proved to be an efficient tool in studying ethylene-derived hydrocarbonaceous species over various silica-supported catalysts. Our findings over the transition metal catalysts largely coincided with earlier works [6, 7]. Half-hydrogenated adsorbed species were predominant, which could be easily hydrogenated off the metal surfaces. However, the copper catalysts were different. A variety of adsorbed species could be identified, among others half-hydrogenated adsorbed species too. They were strongly held and could not be fully removed on hydrogen treatment even at relatively high temperatures.

References

[1] G.A. Somorjai, J. Phys. Chem. 94 (1990) 1013.
[2] A. Fási, J.T. Kiss, B. Török, I. Pálinkó, Appl. Catal. A 200 (2000) 189.
[3] C. de La Cruz, N. Sheppard, J. Chem. Soc., Chem. Commun. (1987) 1854.
[4] S.B. Mohsin, M. Trenary, H.J. Robota, J. Phys. Chem. 92 (1988) 5229.
[5] D.K. Paul, T.P. Beebe, Jr., K.J. Uram, J.T. Yates, Jr., J. Am. Chem. Soc. 114 (1992) 1949.
[6] R.P. Eischens, W.A. Pliskin, Adv. Catal. 10 (1958) 1.
[7] N. Sheppard, C. de La Cruz, Adv. Catal. 41 (1996) 1.