rate was defined as the number of doublings between day 5 and day 9 (determined as the logarithm in base 2 of the increase in the DNA amount) divided by the elapsed time (4 days).

Real-Time quantitative RT-PCR: RNA was extracted from cell layers using Trizol (Life Technologies, Basel, CH) according to the single step acid-phenol guanidinium method,[18] treated with DNAse I using the DNA-free kit (AMS Biotechnology Ltd, CH) and transcribed into cDNA by using random hexamers (Catalys AG, CH) and Stratrascript reverse transcriptase (Stratagene, NL). Real-time RT-PCR reactions were performed and monitored using an ABI Prism 7700 sequence detection system (Applied Biosystems, Rotkreuz, Switzerland). In the same reaction, cDNA samples were analyzed both for the gene of interest and the reference housekeeping gene (18-S rRNA), by using a multiplex approach (Perkin Elmer User Bulletin No. 2). The probe for 18-S rRNA was fluorescently labeled with VIC and TAMRA (Applied Biosystems), whereas probes for the genes of interest were labeled with 6-carboxy-fluorescein (FAM) and TAMRA. The efficiency of each set of primers and probes, assessed as previously described,[19] was always higher than 90%. Primers were purchased from Microsynth (Balgach, CH) and probes were from Perkin-Elmer or Eurogentech (Seraing, B).

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[1] a) A. Berlin in *Electrical and Optical Polymer Systems: Fundamentals, Methods and Applications* (Eds.: D. L. Wise, G. E. Wnek, D. J. Trantolo, T. M. Cooper, J. D. Gresser), Marcel Dekker Inc., New York, **1998**, pp. 47–95; b) H. Shirakawa, *Angew. Chem.* **2001**, *113*, 2642–2648; *Angew. Chem. Int. Ed.* **2001**, *40*, 2574–2580; c) A. G. MacDiarmid, *Angew. Chem.* **2001**, *113*, 2649–2659; *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590; d) A. J. Heeger, *Angew. Chem.* **2001**, *113*, 2660–2682; *Angew. Chem. Int. Ed.* **2001**, *40*, 2591–2611.
[2] R. V. Gregory, W. C. Kimbrell, H. H. Kuhn, *Synth. Met.* **1989**, *28*, C823–C835.
[3] A. Guiseppi-Elie, J. M. Tour, D. L. Allara, N. F. Sheppard, *Mater. Res. Soc. Symp. Proc.* **1996**, *413*, 439–444.
[4] T. Livache, A. Roget, E. Dejean, C. Barthet, G. Bidan, R. Téoule, *Nucl. Acid Res.* **1994**, *22*, 2915–2921.
[5] S. Ibrahim, C. Pickett, C. Sudbrake, *J. Electroanal. Chem.* **1995**, *387*, 139–142.
[6] V. Shastri, PhD Dissertation, Rensselaer Polytechnic Institute **1995**.
[7] a) R. Langer, *Nature* **1998**, *392 (suppl.)*, 5–10; b) R. Langer, J. B. Vacanti, *Science* **1993**, *260*, 920–926.
[8] C. Schmidt, V. Shastri, J. Vacanti, R. Langer, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 8948–8956.
[9] a) Y. Hong, L. L. Miller, *Chem. Mater.* **1995**, *7*, 1999–2000; b) A. Donat-Bouillud, L. Mazerolle, P. Gagnon, L. Goldenberg, M. C. Petty, M. Leclerc, *Chem. Mater.* **1997**, *9*, 2815–2821.
[10] T. V. Vernitskaya, O. N. Efimov, *Russ. Chem. Rev.* **1997**, *66*, 443–457.
[11] V. Shastri, N. Rahman, I. Martin, R. Langer, *Mater. Res. Soc. Symp. Proc.* **1999**, *550*, 215–219.
[12] A. N. Zelikin, P. Shastri, R. Langer, *J. Org. Chem.* **1999**, *64*, 3379–3380.
[13] J. R. Reynolds, P. A. Poropatic, R. L. Toyooka, *Macromolecules* **1987**, *20*, 958–961.
[14] K. Leong, P. D'Amore, R. Langer, *J. Biomed. Mater. Res.* **1986**, *20*, 51–64.
[15] A. Muraglia, I. Martin, R. Cancedda, R. Quarto, *Bone* **1998**, *22*, 131S–134S.
[16] J. Wong, D. Ingber, R. Langer, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 3201–3204.
[17] C. Maniatopoulos, J. Sodek, A. H. Melcher, *Cell Tissue Res.* **1988**, *254*, 317–330.
[18] P. Chomczynski, N. Sacchi, *Anal. Biochem.* **1987**, *162*, 156–159.
[19] I. Martin, M. Jakob, D. Schafer, W. Dick, G. Spagnoli, M. Heberer, *Osteoarthritis Cart.* **2001**, *9*, 112–118.

Characterization of C_2 (C_xH_y) Intermediates from Adsorption and Decomposition of Methane on Supported Metal Catalysts by in situ INS Vibrational Spectroscopy[**]

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Conversion of methane into higher hydrocarbons is a process of enormous technological importance, which would benefit from a better understanding of the nature of the surface intermediates formed during methane activation. Currently methane is converted into hydrocarbons mainly by an indirect route[1, 2] via syn gas[3] as the intermediate. Alternative routes, such as oxidative coupling of methane[4–7] over metal oxide catalysts and methane homologation[8–10] on transition metal catalysts have also been extensively investigated. In a previous study we[11] have observed the formation of various C_xH_y surface intermediate species after methane decomposition on single-crystal Ru(0001) and Ru(1120) model catalysts, observed by high-resolution electron energy loss spectroscopy (HREELS). In this study we used INS to investigate the surface intermediate species formed during the decomposition of methane on Ru/Al_2O_3 and Ni/SiO_2 catalysts. We relate these findings to our previous work on idealized single-crystal model catalysts. The present work represents a step in the effort to bridge the gap between surface science and real-world catalysts in terms of the type of material and pressure used. Inelastic neutron scattering (INS)[12–14] vibrational spectroscopy is a technique that can be directly applied to high surface-area catalysts from ambient to high pressures. This method can also provide accurate quantitative information, has high sensitivity to hydrogenous species, and is not limited by the selection rules of other vibrational spectroscopies.

Herein we report the first experimental evidence of the formation of ethylidyne, vinylidene, and methylidyne (C_xH_y) species from methane on supported metal catalysts. Shown in Figure 1 is the difference INS vibrational spectrum after methane decomposition on Ru/Al_2O_3. The rather modest resolution, especially at higher frequencies, and poor statistics are the result of having to use a difference spectrum and of the relatively small amount of H in the sample. Nonetheless, the

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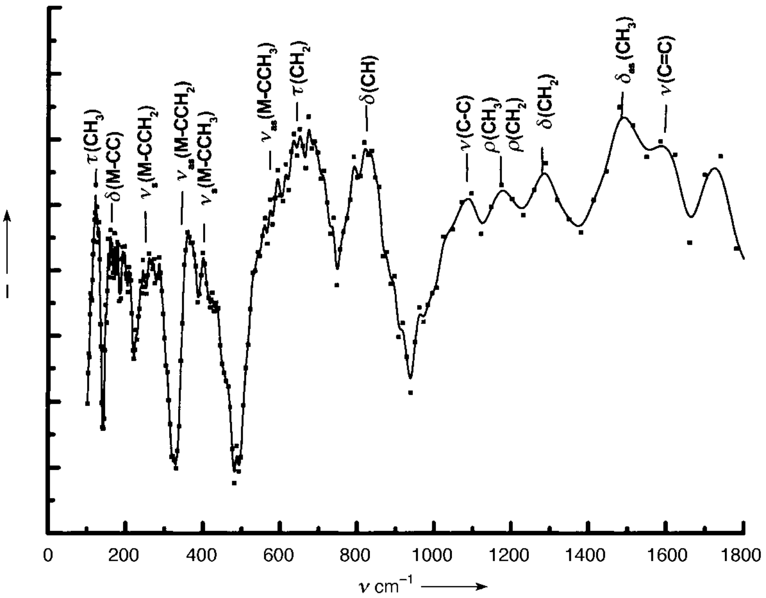

Figure 1. INS spectrum obtained after methane decomposition over Ru/Al_2O_3 at 250 °C, some tentative assignments are shown. (The line is drawn to guide the eye).

spectrum clearly reveals the presence of the C_2 species in addition to CH. Our assignments are made with reference to work on model compounds as well as the previous HREELS study[11] on single-crystal surfaces. Thus, we tentatively assign the bands at approximately 120, 400, 570, 1085, 1165, 1485 cm^{-1} to modes of the ethylidyne species, namely $\tau(CH_3)$, $\nu_s(M{-}CCH_3)$, $\nu_{as}(M{-}CCH_3)$, ν(C–C), $\rho(CH_3)$, and $\delta_{as}(CH_3)$, respectively (M is the surface metal atom, namely Ni or Ru). For the vinylidene species we observe bands at 200, 280, 360, 670, 1220, and 1300 and cm^{-1} which we attribute to δ(M–CC, $\nu_s(M{-}CCH_2)$, $\nu_{as}(M{-}CCH_2)$, $\tau(CH_2)$, $\rho(CH_2)$, and $\delta(CH_2)$, respectively. Other CH_2 deformation modes are contained in the broad band above 1450 cm^{-1} and the ν(C=C) mode appears at approximately 1580 cm^{-1}. The peak at 830 cm^{-1} may be assigned to the CH bending mode of methylidyne. M–C stretching modes for methylidyne should also be observable and are assumed to be contained in the broad bands below 500 cm^{-1}. Computational studies are in progress to aid in the detailed assignment of the M–C stretching and other modes of these intermediate species. The observation of the methylidyne species (CH) at 830 cm^{-1} is in good agreement with earlier studies which reported that other methyl intermediates decompose below 202 °C to produce the CH species.[15] Summarized in Table 1 are the INS vibrational frequencies and tentative mode assignments for the three C_xH_y (vinylidene, ethylidyne, and methylidyne) species on the supported Ru and Ni catalysts. It is worth noting that we find features similar to those on Ru/Al_2O_3 for the Ni/SiO_2 catalysts although the ethylidyne species has rarely been observed on Ni surfaces.[16] Our assignments of modes of the vinylidene and ethylidyne species are in excellent agreement with our previous work on Ru(1120) model catalysts[11] (Table 1).

At the higher decomposition temperature of 325 °C we find that the bands assigned to the ethylidyne species decrease in intensity relative to those of vinylidene, most notably $\tau(CH_3)$, $\nu_s(M{-}CCH_3)$, $\nu_{as}(M{-}CCH_3)$, ν(C–C), and the deformation modes of $\delta(CH_3)$. For the vinylidene species the intensities of $\nu_s(M{-}CCH_2)$, $\nu_{as}(M{-}CCH_2)$, $\delta_s(CH_2)$, and ν(C=C) are higher at 325 °C which clearly suggests that this C_2 intermediate is more stable at higher temperatures than ethylidyne. This result is in good agreement with methane decomposition studies on Ru(1120)[11, 17] where the ethylidyne species was found to exist only at low temperature and was found to transform to vinylidene species on heating. Experimental

Table 1. INS vibrational frequencies [cm^{-1}] and mode assignments for various C_xH_y intermediates on supported metal (Ni, Ru) catalysts, single-crystal surfaces (HREELS), and model compounds (IR).

Methylidyne Mode assignment	Ni[a]	Ru[a]	Surface Ru(1120)[11]	Ni(111)[18]	$[Ru_3(\mu_3CH)H_3(CO)_9]$[23]
δ(CH)	890	830	830	790	894

Vinylidene Mode assignment	Ni[a]	Ru[a]	Ru(1120)[11]	Surface Ru(0001) [11]	O/Ru(0001)[19]	$[Os_3H_2(CCH_2)(CO)_9]$[20]
δ(M–CC)	184	200				
$\nu_s(M{-}CCH_2)$	283	280				255
$\nu_{as}(M{-}CCH_2)$	375	360	345		455	311
$\tau(CH_2)$	672	670				
$\rho(CH_2)$	1260	1220				
$\delta(CH_2)$	1310	1300	1410	1395	1435	1328
ν(C=C)	1600	1580	1620	1160	1435	1467

Ethylidyne Mode assignment	Ni[a]	Ru[a]	Pt black[21]	Co_3-C-CH_3[22]
δ(M–CC)	184	200		220
$\tau(CH_3)$	125	120		
$\nu_s(M{-}CCH_3)$	432	400	400	403
$\nu_{as}(M{-}CCH_3)$	605	570	(645)	548
ν_{as}(C–C)	1040	1085	1130	1162
$\rho(CH_3)$	1184	1165	985	1004
$\delta_{as}(CH_3)$	1477	1485		1420

[a] The present work.

investigations are in progress to acquire further insights regarding the nature of the intermediates under various reaction conditions.

Experimental Section

Methane decomposition was carried out for 4 h on pre-reduced samples of 10% Ni/SiO_2 and 10% Ru/Al_2O_3 at 250° and 325 °C in separate reactors. Each of these was subsequently quenched in a liquid-nitrogen bath. The reactors were then mounted in a closed-cycle refrigerator and INS spectra were collected at −253 °C on the filter difference spectrometer (FDS) instrument at the Lujan Center at Los Alamos National Laboratory. Data were treated by deconvolution of the instrumental resolution function[24] and subtraction of spectra of identical starting samples. Some of the experiments were repeated and an excellent reproducibility was observed.

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[1] G. P. Van der Laan, A. A. C. M. Beenackers, *Catal. Rev. Sci. Eng.* **1999**, *41*, 255–318.

[2] F. J. Keil, *Microporous Mesoporous Mater.* **1999**, *29*, 49–66.

[3] J. R. Rostrup-Nielsen in *Catalytic Steam Reforming*, *Vol. 5* (Eds.: J. R. Anderson, M. Boudart), Springer, Berlin, **1984**.

[4] G. E. Keller, M. M. Bhasin, *J. Catal.* **1982**, *73*, 9–19.

[5] J. S. Lee, S. T. Oyama, *Catal. Rev. Sci. Eng.* **1988**, *30*, 249–280.

[6] J. H. Lunsford, *Catal. Today*, **1990**, *6*, 235–259.

[7] V. R. Choudhary, S. T. Chaudhari, A. M. Rajput, V. H. Rane, *J. Chem. Soc. Chem. Commun.* **1989**, 1526–1527.

[8] T. Koerts, R. A. van Santen, *J. Chem. Soc. Chem. Commun.* **1991**, 1281–1283.

[9] M. Belgued, P. Pareja, A. Amariglio, H. Amariglio, *Nature* **1991**, *352*, 789–790.

[10] M. M. Koranne, G. W. Zajac, D. W. Goodman, *Catal. Lett.* **1995**, *30*, 219–234.

[11] M. C. Wu, D. W. Goodman, *J. Am. Chem. Soc.* **1994**, *116*, 1364–1371, and references therein.

[12] R. R. Cavanagh, R. D. Kelley, J. J. Rush in *Vibrational Spectroscopy of Molecules on the Surface*, *Vol. 1* (Eds.: J. T. Yates, T. E. Madey), Plenum, New York, **1987**.

[13] E. F. Sheka, *Physica B* **1991**, *174*, 227–232.

[14] J. Eckert, *Spectrochimica Acta. A* **1992**, *48*, 271–283.

[15] M. B. Lee, Q. Y. Yang, S. T. Ceyer, *J. Chem. Phys.* **1987**, *87*, 2724–2741.

[16] M. P. Lapinski, J. G. Ekerdt, *J. Phys. Chem.* **1992**, *96*, 5069–5077.

[17] M. C. Wu, P. L. Solomun, D. W. Goodman, *J. Vac. Sci. Technol.* **1994**, *12*, 2205–2209.

[18] S. Lehwald, H. Ibach, *Surf. Sci.* **1979**, *89*, 425–445.

[19] M. M. Hills, J. E. Parmeter, W. H. Weinberg, *J. Am. Chem. Soc.* **1987**, *109*, 597–599.

[20] J. R. Andrews, S. F. A. Kettle, D. B. Powell, N. Sheppard, *Inorg. Chem.* **1982**, *21*, 2874–2877.

[21] R. R. Cavanagh, J. J. Rush, R. D. Kelly, T. J. Udovic, *J. Chem. Phys.* **1984**, *80*, 3478–3484.

[22] P. Skinner, M. W. Howard, I. A. Oxton, S. F. A. Kettle, D. B. Powell, N. Sheppard, *J. Chem. Soc. Fraday Trans.* **1981**, *77*, 1203–1215.

[23] I. A. Oxton, *Spectrochim. Acta A* **1982**, *38*, 181–184.

[24] D. S. Sivia, P. Vorderwisch, R. N. Silver, *Nucl. Instrum. Methods Phys. Res. Sect. A* **1990**, *290*, 492.

Real-time Observation of the H/D Exchange Reaction between Ethylene and Hydrogen on Pt(111)[**]

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Adsorption and reactions of small hydrocarbon molecules on well-characterized metal single-crystal surfaces have been extensively studied to understand heterogeneous catalysis on a molecular level and design more effective catalysts.[1] Deuterated hydrocarbons are frequently used in surface-science studies of hydrocarbon reactions on metal and metal-oxide surfaces. Reaction mechanisms of surface reactions can be better understood by observing H/D reaction products and the kinetic isotope effect. The H/D exchange products on the surface have been analyzed using several different techniques including thermal desorption spectroscopy (TPD), laser induced desorption (LID), secondary ion mass spectroscopy (SIMS), and vibration spectroscopy. The H/D exchange product distribution is often difficult to determine reliably if a molecule undergoes multiple H/D substitution. The H/D substituted molecules are too similar in their spectroscopic features to identify accurately by using vibration spectroscopy. SIMS, TPD, and LID data are often very confusing because of the fragmentation of molecules on the surface or in a mass spectrometer. Fragmentation makes it difficult to quantitatively identify multiply deuterated hydrocarbon species on the surface.

We investigated the reaction of C_2D_4 and H on a Pt(111) surface using a Cs^+-ion reactive ion scattering (RIS) method. We successfully identified $C_2D_{4-x}H_x$ ($x = 0-4$) species on the surface and observed their concentration change in real time in the temperature range of 200–300 K.

The Cs^+ RIS technique was shown to be an effective method to monitor molecules on surfaces. The experimental details and operating principle for the RIS method can be found elsewhere.[2] Briefly, a Cs^+-ion beam of low energy (10–100 eV) is collided with the surface to be analyzed, and the Cs^+–molecule cluster ions emitted from the surface are analyzed by a mass spectrometer. The Cs^+–molecule cluster ions are formed as the Cs^+-ion projectiles pick up adsorbed

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