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Volume IV: Impact of surface science on catalysis
Structure-selectivity/activity correlations
New routes for catalyst synthesis



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CONTENTS

Impact of surface science on catalysis

D. W. Goodman, Albuquerque, NM/USA Correlations between surface structure and catalytic reactivity for alkane hydrogenolysis over nickel	3— 12	28
K. Christmann, J. Rüstig, Berlin/D Interaction of methanol with nickel, palladium and silver single crystal surfaces	13— 24	28
K. Tamaru, T. Yamada, E. Shincho, C. Egawa, S. Naito, Tokyo/J Different behaviour of adsorbed CO on Ru flat and stepped single crystal surfaces	25— 34	28
A. Brown, J. A. van den Berg, J. C. Vickerman, Manchester/UK Model bimetallic Ru(0001)/Cu catalysts — the influence of surface Cu on the adsorption mode of CO	35— 46	28
N. D. S. Canning, D. A. Outka, R. J. Madix, Stanford, CA/USA States of oxygen on gold surfaces	47— 49	28
T. E. Madey, C. Berndorf, D. L. Doering, S. Semancik, Washington, DC/USA Influence of surface additives, sodium and oxygen, on the structure and bonding of H ₂ O and NH ₃ on Ru(001)	51— 62	28
M. Kiskinova, G. Pirug, H. P. Bonzel, Jülich/D Potassium-promoted NO adsorption and dissociation on a Pt(111) surface	63— 72	28
A. R. McCabe, G. D. W. Smith, Oxford/UK Surface structure, surface composition and reactivity of platinum-rhodium alloy catalysts — investigation by field ion microscopy, atom probe and electron microscopy	73— 84	28
S. Holloway, B. I. Lundqvist, J. K. Nørskov, Göteborg/S and København/DK Electronic factors in catalysis	85— 95	40
R. A. van Santen, Houston TX/USA Coordination to transition metal surfaces — A theoretical study	97—109	40
C. Rong, Wang Hongli, Dalian/P.R. China Trend of activation pattern of diatomic molecules N ₂ , CO and NO on group VIII transition metals	109—119	40
T. Matsushima, Sapporo/J On the mechanism of the CO oxidation on Pt(111) surfaces at low temperatures and the angular distribution of the product desorption	121—131	40
M. Grunze, M. Golze, J. Fuhler, M. Neumann, E. Schwarz, Berlin/D, Orono, MA/USA, Osnabrück/D The intermediates in nitrogen dissociation on rhenium and iron surfaces	133—143	40
H. Körner, H. Landes, G. Wedler, H. J. Kreuzer, Erlangen/D and Halifax/CND Model study of the Boudouard reaction on iron	145—156	40

	Volume IV Page	Programme Page
R. A. Hubert, J. M. Gilles, Namur/B Physical Characterization of a Fe/MgO(001) model catalyst	157—171	40
W. Palczewska, I. Ratajczykowa, I. Szymerska, M. Krawczyk, Warszawa/PL Lead and carbon monoxide as additives modifying the selectivity of palladium catalysts in partial hydrogenation of acetylenes	173—183	40
J. Massardier, B. Tardy, P. Delichere, M. Abon, J. C. Bertolini, Villeurbanne/F Pt-Ni(111) single crystal alloys: surface reactivity with respect to pure metals	185—195	40
R. G. Greenler, B. E. Hayden, K. Kretzschmar, R. Klausner, A. M. Bradshaw, Berlin/D A comparison of the frequencies of CO molecules adsorbed on Pt(111), on stepped Pt(111) and on kink-stepped Pt(111)	197—207	40
G. Kirch, E. Schwab, E. Wicke, H. Züchner, Münster/D Characterization by AES and SIMS of segregation catalysts for ammonia synthesis, prepared from TiFe and TiRu	209—218	40
W. Benecke, R. Schulz, H.-G. Feller, M. Ralek, Berlin/D XPS- and SIMS-investigations of the surface composition of manganese/iron alloy catalysts for the Fischer-Tropsch synthesis	219—227	40
F. Chehab, W. Kirstein, F. Thieme, Hamburg/D Hydrogen spill over on Ni-rich Cu-Ni single crystal surface?	229—237	41
C. T. Au, M. W. Roberts, Cardiff/UK A photoelectron spectroscopic study of the adsorption and catalytic decomposition of formic acid at Zn(0001) and Zn(0001)-O surfaces	239—250	41
W. Hirsch, D. Hofmann, W. Hirschwald, Berlin/D Interaction of CO, C ₂ H ₄ , CH ₃ OH and HCOOH with single crystal faces of ZnO and ZnO(Cu) catalyst surfaces studied by surface spectroscopies	251—262	41
W. E. Brower, Jr., K. M. Simon, W. Kowbel, E. E. Alp, Carbondale IL/USA Evaluation of the catalytic behaviour of metallic glasses via thermal analysis, Moessbauer spectroscopy and electron microscopy	263—272	41
Structure-selectivity/activity correlations		
W. K. Hall, R. L. Schneider, J. Goldwasser, Milwaukee, WI/USA Reaction of cyclopropanes over molybdena-alumina and related catalyst systems	273—284	26
A. Miyamoto, K. Mori, M. Inomata, Y. Murakami, Nagoya/J Dispersion — selectivity/activity correlations for supported vanadium oxides	285—296	26
A. J. van Hengstum, J. G. van Ommen, H. Bosch, P. J. Gellings, Enschede/NL Selective oxidation of methanol and o-xylene by V ₂ O ₅ on TiO ₂ catalysts	297—307	26
B. Coq, F. Figueras, J. Jupille, C. Leclercq, G. Picquard, M. Ruiz, A. Thierri-Sorel, Montpellier, Villers sur les Nancy and Villeurbanne/F Catalytic oxidation of furfural and furan over molybdenum-vanadium mixed oxides	309—319	26
E. Rorris, J. B. Butt, R. L. Burwell, Jr., J. B. Cohen, Evanston, IL/USA Structure sensitivity of propylene hydrogenation over silica-supported platinum and palladium	321—331	26

	Volume IV Page	Programme Page
A. Masson, B. Bellamy, G. Colomer, M. M'Bedi, P. Rabette, M. Che, Paris/F Structure sensitivity of ethylene hydrogenation on platinum particles deposited by the atomic beam method onto amorphous silica	333—344	26
N. Poole, D. A. Whan, Edinburgh/UK Exchange of cyclopentane and methylcyclopentane on platinum in Y-type zeolite	345—355	26
P. A. Jacobs, M. Tielen, Leuven/B Investigation of shape selectivity effects in medium pore H/Pt-zeolites: product distributions from cyclodecane	357—369	22
G. A. Martin, J. A. Dalmon, C. Mirodatos, Villeurbanne/F Particle size-sensitivity in catalysis by nickel: a statistical approach based on the combined effect of surface coverage and active site dimension	371—380	26
<u>Molybdenum-based catalysts</u>		
Y. Iwasawa, H. Tanaka, Yokohama/J Cooperative catalysis by active SiO ₂ -attached Mo-dimers in ethanol oxidation	381—392	48
D. Kalló, J. Engelhardt, Budapest/H Kinetics of the interconversion of n-butenes over reduced molybdena- alumina catalysts	393—402	48
W. M. Keely, P. Jerus, E. K. Dienes, A. L. Hausberger, Louisville KY/USA Preparation techniques of hydrotreating catalysts and their influence on the location of the metal oxides and performance	403—414	48
M. Houalla, C. L. Kibby, E. L. Eddy, L. Petrakis, D. M. Hercules, Pittsburgh PA/USA Structure and reactivity of promoted and unpromoted molybdena alumina catalysts	415—425	48
K. F. McCarty, G. L. Schrader, Ames IA/USA Reduced molybdenum states in hydrodesulfurization: investigations using chevre phase catalysts	427—438	48
G. V. Smith, C. C. Hinckley, T. Nishizawa, N. Yoshida, M. Saporoschenko, R. H. Shiley, Carbondale and Champaign, IL/USA Sensitivity of dehydrogenation, dehydration, and desulfurization for surface stoichiometry and structure of iron sulfides	439—450	48
<u>Oxidation reactions</u>		
J. C. Volta, J. M. Tatibouet, C. Pichitkul, J. E. Germain, Villeurbanne/F Structural-sensitive catalytic oxidation on MoO ₃ catalysts	451—461	48
H. Yu. Kutyrev, A. A. Firsova, V. A. Matyshak, L. Ya. Margolis, Moscow/USSR Intermediate forms of selective olefin oxidation and structures of complex molybdenum oxide catalysts	463—472	48
I. Matsuura, Toyama/J Surface phase of vanadium — phosphorus oxide catalyst for n-butene and n-butane oxidation to maleic anhydride	473—484	48
N. S. Kozlov, G. V. Isagulians, E. A. Skrigan, I. P. Belomestnykh, G. V. Milorava, G. V. Shakhnovich, L. A. Kupcha, Moscow and Minsk/USSR Structure and activity of vanadium catalysts in combined synthesis of styrene and aniline	485—496	48

	Volume IV Page	Programme Page
I. Apostol, J. Haber, T. Miodnicka, J. Poltowicz, Kraków/PL Selectivity-electronic structure correlations in liquid phase cooxidation of aldehydes and olefins in the presence of cobalt porphyrins as catalyst	497—506	48
<u>Silicates and zeolites</u>		
K.-P. Wendlandt, H. Bremer, Merseburg/DDR Catalytic behaviour of aluminosilicates and the HSAB principle	507—517	49
K. G. Ione, L. A. Vostrikova, A. V. Petrova, V. M. Mastikhin, Novosibirsk/USSR Catalytic properties of crystalline silicates of group I-VIII elements	519—529	49
A. G. Ashton, I. E. Elliott, J. Dwyer, F. R. Fitch, F. J. Machado, Manchester /UK Catalysis and surface composition of modified zeolites	531	49
M. Nitta, M. Yamashita, M. Shiotani, K. Aomura, Y. Nozawa, M. Hatano, Sapporo and Sendai/J The differences in acidity between high-silica zeolites characterized by calorimetry, ESR, and MASNMR	533—543	49
D. Fraenkel, M. Cherniavsky, M. Levy, Rehovot/IL Evidence for the involvement of two sieving effects in the catalytic alkylation of aromatics over HZSM5-type zeolites	545—554	49
H. Chon, B. J. Ahn, S. E. Park, Seoul/Korea Shape selectivity of ZSM-5 and ZSM-8 type zeolite catalysts	555—564	49
<u>Bimetallic catalysts</u>		
Lin Liwu, Zang Jingling, Wu Rongan, Wang Chengyu, Du Hongzhang, Dalian/P.R. China The active sites on Pt-Sn catalysts and their selectivity in n-heptane reaction	565—576	49
G. C. Bond, Xu Yide, Uxbridge/UK Reversible formation of supported ruthenium-copper clusters by oxidation and reduction	577—585	49
A. K. Datye, J. Schwank, Ann Arbor MI/USA Characterization of bimetallic ruthenium-gold catalysts by analytical electron microscopy and test reactions	587—598	49
Guo Xiexian, Xin Qin, Li Yongxue, Jin Dai, Ying Pinliang, Dalian/P.R. China Investigation of Cu-clustering and metal-support interaction effects for Ru-Cu-SiO ₂ catalysts	599—610	49
S. De Rossi, A. Cimino, M. Lo Iacono, G. Ferraris, Rome/I Propene hydrogenation on copper-zinc on alumina	611—622	49
<u>Miscellaneous systems</u>		
K. Balasubramanian, J. C. Kuriacose, Madras/IND Activity and selectivity of zinc chromium ferrite for the dehydrogenation of 2-propanol	623—634	49
S. Tsuchiya, A. Fukui, M. Hara, H. Imamura, Ube/J Structure-selectivity for hydrogenation and isomerization of some graphite intercalation compounds	635—646	49

	Volume IV Page	Programme Page
H.-D. Eichhorn, C. Jäckh, W.-D. Mroß, H. Schuler, Ludwigshafen/D Activity and selectivity relationship in the oxychlorination of ethylene on $\text{CuCl}_2\text{-KCl}/\gamma\text{-Al}_2\text{O}_3$ -catalysts	647—656	49
New routes for catalyst synthesis		
B. V. Romanovsky, Moscow/USSR Immobilization of transition metal complexes on inorganic supports	657—667	29
G. V. Lisichkin, A. Ya. Yuffa, G. V. Kudryavtsev, Moscow and Tumen/USSR New methods for chemical modification of silica in synthesis of heterogeneous metal complex catalysts	669—679	29
S. L. Suib, J. C. Baxter, Storrs, CT/USA Photochemical studies of metal carbonyls in zeolites	681—687	24
Y. Doi, K. Yano, K. Yokota, H. Miyake, K. Soga, Yokohama/J Synthesis and catalysis of ruthenium clusters anchored to silica	689—700	24
M. Niwa, S. Morimoto, M. Kato, T. Hattori, Y. Murakami, Nagoya/J Fine control of pore size of H-mordenite by vapor-phase deposition of $\text{Si}(\text{OCH}_3)_4$	701—711	41
E. Moretti, G. Leofanti, M. Padovan, M. Solari, G. De Alberti, F. Gatti, Milano/I A new route to ZSM-5 zeolite: crystal properties and catalytic activity evolution during the synthesis	713—723	41
M. L. Ocelli, V. N. Parulekar, J. W. Hightower, Pittsburgh PA and Houston TX/USA Sorption of normal paraffins in a pillared clay mineral	725—733	41
J. Shabtai, F. E. Massoth, M. Tokarz, G. M. Tsai, J. McCauley, Salt Lake City UT/USA Characterization and molecular shape selectivity of cross-linked montmorillonite (CLM) catalysts	735—745	41
M. Camia, P. Gherardi, G. Gubitosa, M. Petrera, N. Pernicone, Novara/I IRS study of competitive adsorption of ammonia and pyridine on ZSM-5 zeolites	747—758	41
S. Tanabe, A. Ueno, Y. Kotera, K. Tohji, Y. Udagawa, Aichi/J Study on the elementary steps of Ni/SiO_2 catalyst preparation by means of EXAFS	759—768	41
J. Klein, W. Behrens, B. Kretzschmar, H.-J. Steinert, K.-D. Vorlop, Braunschweig/D Heterogeneous biocatalysis with whole microbial cells immobilized in polymeric carriers	769—780	29
K. Jerábek, K. Setinek, Prague/CSSR Assessment of steric influence in reactions on polymer-bound catalysts	781—789	41
J. Turkevich, Z. Xu, Princeton, NJ/USA Catalytic activity of complexes formed by platinum anticancer drugs	791—801	29
K.-H. Stadler, H. P. Boehm, Munich/D The photochemical deposition of noble metals onto n-type semiconductors	803—814	24
A. Morikawa, T. Nakajima, I. Nishiyama, K. Otsuka, Tokyo/J Catalysis of photoprepared niobium oxide catalyst for dimerization and isomerization of olefins	815—826	24

	Volume IV Page.	Programme Page
M. Stoukides, C. G. Vayenas, Cambridge MA/USA Electrochemical modification of the activity and selectivity of silver for light olefin oxidation	827—833	41
M. Yamada, K. Itabashi, Tokyo/J Preparation and catalytic properties of alumina films by anodic oxidation of aluminum	835—846	41
I. A. Zrunchev, T. F. Popova, Sofia/BG Catalytic processes in magnetic structured catalyst beds. New trend of catalysis	847—858	42
V. V. Lunin, A. Z. Khan, L. A. Erivanskaya, O. V. Chetina, G. V. Antoshin, E. S. Shpiro, Kh. M. Minachev, Moscow/USSR Investigation of catalytic systems derived from the intermetallics of $ZrCr_2$, $ZrMo_2$, ZrW_2 and their hydrides of $ZrCr_2H_{3.6}$, $ZrMo_2H_{0.8}$, $ZrW_2H_{1.8}$	859—870	42
I. Ravet, A. Gourgue, Z. Gabelica, J. B. Nagy, Namur/B Hydrogenation activity of colloidal cobalt boride particles prepared from reversed micelles CTAB-1-hexanol-water	871—878	42
S. Matsuda, A. Kato, M. Mizumoto, H. Yamashita, Ibaraki/J A new support material for catalytic combustion above 1000 °C	879—889	42
Ch. Travers, J. P. Bournonville, G. Martino, Rueil-Malmaison/F New route to Rh-Sn bimetallic catalysts selective for the hydrogenation of esters into alcohols	891—902	42
J. Margittfalvi, M. Hegedűs, S. Göbölös, E. Kern-Tálas, P. Szdlacsek, S. Szabó, F. Nagy, Budapest/H Controlled surface reactions for preparation of Sn-Pt/ Al_2O_3 catalysts	903—914	42
Author Index	A-1 — A-19	

Impact of surface science on catalysis

Correlations Between Surface Structure and Catalytic Reactivity for Alkane Hydrogenolysis Over Nickel

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Summary

Kinetic studies over different crystal planes of nickel show the hydrogenolysis of n-butane to be structure sensitive. Significant differences in product formation rates are observed between the Ni(111) and the Ni(100) surfaces. The open (100) surface demonstrates a much higher activity toward rupturing carbon-carbon bonds than does the (111) surface. These results together with previous studies on ethane and cyclopropane hydrogenolysis confirm this result to be a general one. Furthermore an excellent comparison of the product distribution as a function of temperature between a Ni(100) catalyst and a polycrystalline nickel catalyst suggest that (100) facets dominate the chemistry of the polycrystalline surface.

Introduction

The hydrogenolysis of saturated hydrocarbons, or the rupture of carbon-carbon bonds by hydrogen, is well-known to be structure-sensitive, that is their rates per surface metal atom vary with the percentage of metal exposed on the catalyst [1]. Various interpretations for this structure-sensitivity have been offered, many of which are based upon geometric arguments. Assuming that geometric considerations do play a significant, if not dominant, role in giving rise to the structure-sensitivity of certain surface catalytic reactions, then the effect should be amenable to quantification using different orientations of metal single crystal catalysts.

Integrating in a single apparatus surface analytical techniques with the ability to study reaction kinetics at elevated pressures has proved to be quite useful in correlating structural and compositional changes with reaction dynamics [2,3]. Specifically,

for several reactions excellent comparisons have been made between rates and activation energies measured for single crystal catalysts and those observed for high-area, supported catalysts [2]. These reactions, methanation of CO [3] and CO₂ [4], and hydrogenation of ethylene [5] are known to be structure-insensitive reactions. The chemistry manifested on different facets has been found to be indistinguishable. In contrast, recent results for ethane [6] and cyclopropane [7] hydrogenolysis over different facets of nickel have shown marked differences in rates and activation energies. These differences were ascribed to the apparent superior ability of the "open" Ni(100) surface to cleave carbon-carbon bonds compared to the more densely packed Ni(111) surface. It was suggested that the tendency of the (100) surface to promote hydrogenolysis more rapidly than the (111) surface was related to the relative spacings between the high coordination sites on the two planes, the spacing on the (111) surface being close to a carbon-carbon bond distance whereas the spacing on the (100) surface is considerably larger. On the (111) surface the carbon-carbon bonds can remain intact yet bond in the high coordination sites, those sites believed to accommodate the most stable bonding [8]. This is not the case for the (100) surface, therefore a driving force exists on this surface for breaking carbon-carbon bonds and allowing the individual carbons to migrate to the preferred high coordination bonding sites. This interpretation suitably explains the general experimental observation that on high-area, supported catalysts, a reduction in activity is associated with an increase in particle size. Sintering to larger particles is expected to yield a larger proportion of (111) surfaces, the thermodynamically more stable surface. Since the ratio of the open surfaces to the (111) surfaces falls with an increase in particle size, the hydrogenolysis rate will accordingly fall. Of great interest to this interpretation is the question of its applicability to other hydrogenolysis reactions. With this in mind we have carried out similar studies for n-butane and cyclopropane hydrogenolysis. The results for cyclopropane have been reported in detail elsewhere [7]. Here we will concentrate on the n-butane hydrogenolysis data and their implication to the reaction mechanism of alkane hydrogenolysis in general.

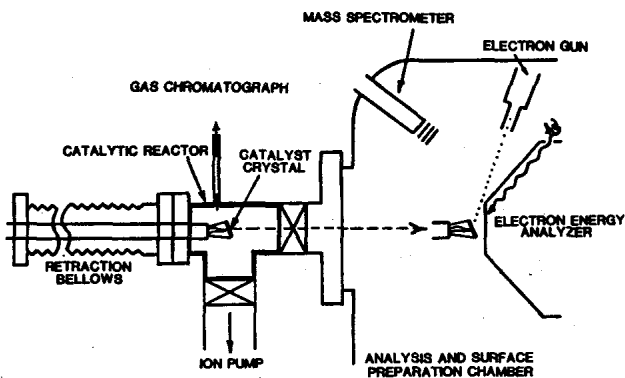


Figure 1. A schematic of the surface analysis/microcatalytic reactor used in these studies.

Experimental

The apparatus for this work is shown in Fig. 1. It consists of two bakeable ultra-high vacuum chambers, connected by a metal valve and separately pumped. The base pressure in the analysis chamber and the reactor is 10^{-10} Torr. The single crystals of nickel ($\sim 1.0 \text{ cm}^2$ surface area) are mounted on tungsten leads and heated resistively. The sample is mounted on a retraction bellows and can be translated horizontally to various positions in either chamber. The samples were cleaned by oxidation at 1400K in 10^{-6} Torr O_2 followed by reduction at 800K in 5 Torr H_2 . A typical Auger spectrum of a clean nickel surface is given in Refs. [3] and [10]. High purity hydrogen was used in all kinetic measurements. The n-butane was triply distilled from a low temperature bath to assure purity.

Results and Discussion

Fig. 2a shows the specific reaction rate (product molecules/substrate surface atom/s) or turnover frequency (TF) for methane formation from n-butane over a Ni(100) catalyst plotted in Arrhenius form. The values shown are for a $\text{H}_2/\text{n-butane}$ ratio of 100 and a total pressure of 100 Torr. At a given temperature the

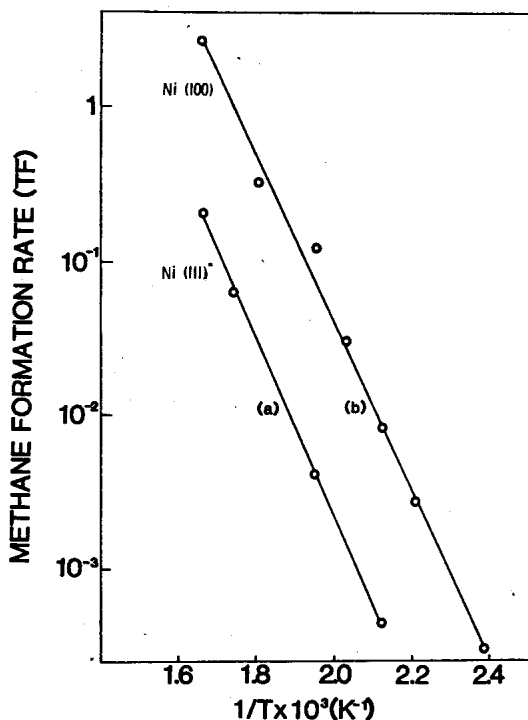


Figure 2. A comparison of n-butane hydrogenolysis over single crystals of nickel. Pressure = 100 Torr. H_2 /n-butane ratio = 100.

rate of methane production over an initially clean crystal was constant in time with no apparent induction period. No self-poisoning was observed for reaction periods of hours and extensive conversions. The carbon level during reaction remains constant at a submonolayer coverage as determined by Auger spectroscopy. The turnover frequency (CH_4 /Ni surface atom/s) during a fixed time (typically 1000s) was determined using the Ni(100) atom density of 1.62×10^{15} atoms/cm².

The slope of the line obtained for the Ni(100) data corresponds to an activation energy of 25 kcal/mole. This value as well as the measured rates are close to the activation energies and rates

found for the methanation reaction as well as ethane hydrogenolysis over this surface. This close comparison between activation energies and rates suggest that these reactions over a Ni(100) catalyst are following the same reaction pathway and are limited by the same reaction step. For methanation it has been shown [11] that the reaction rate is determined by a delicate balance of the surface carbide formation step and the step involving its removal by surface hydrogen. Both ethane and n-butane hydrogenolysis on this surface then likely involve a similar single-atom, surface carbon formation step followed by its reduction by hydrogen and these steps control the kinetics.

Anderson has proposed [13] that the reaction rate for ethane hydrogenolysis is methane formation controlled because of the similarities in the temperature dependence of the hydrogenolysis rates and the rates of deuterium/hydrogen exchange. This mechanism could entail first the formation of a single-atom, (partially hydrogenated), carbonaceous species followed by hydrogen reduction to methane--precisely the methanation mechanism. For hydrogenolysis then, we propose that the reaction enters the methanation sequence at the rate-limiting, carbon-hydrogenation point.

Figure 2b shows the kinetic data for n-butane hydrogenolysis over a Ni(111) catalyst at identical conditions as for those data of Figure 2a. These data, as well, are steady-state values with no evidence of self-poisoning. As observed for the (100) catalyst, the carbon level during reaction remained constant at a submonolayer coverage. The specific rate was determined using the Ni(111) atom density of 1.88×10^{15} atoms/cm². It is evident that the activity of the Ni(111) surface toward n-butane hydrogenolysis to methane is considerably less than that observed for the (100) surface. A similar lower activity was seen for the (111) surface compared to the (100) surface for ethane [6] and cyclopropane [7] hydrogenolysis. The degree of inactivity of the (111) facet is uncertain at this point because edge effects and surface defects could contribute to the residual activity. It is clear, however, that the intrinsic activity of the (100) surface far exceeds that of the (111) surface for rupturing carbon-carbon bonds. Without data for other crystal facets we cannot state that all activity of a polycrystalline particle is due to (100) surfaces; however, the data do suggest this to be the case.

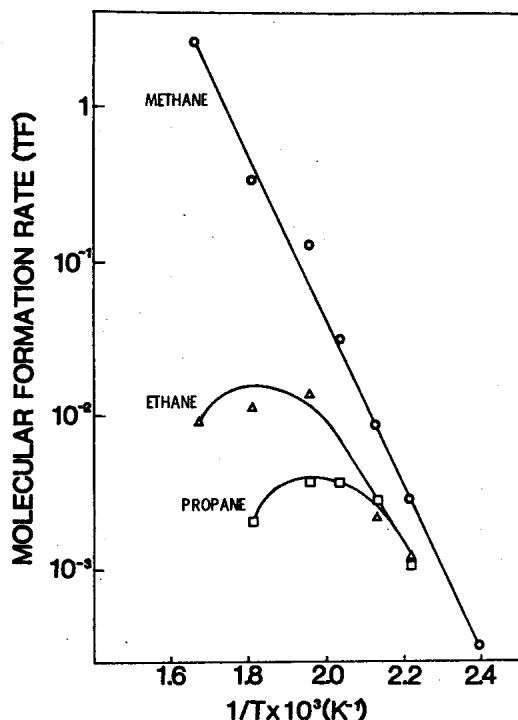


Figure 3. Hydrogenolysis of n-butane over a Ni(100) single crystal catalyst. Pressure = 100 Torr. H_2/n -butane ratio = 100.

Figure 3 shows the product distribution from n-butane hydrogenolysis on a Ni(100) catalyst as a function of reaction temperature. As is observed for a polycrystalline [13] catalyst, higher temperatures lead to a preference for methane product. Of great interest regarding the question of the relative contribution of (100) surfaces to total product formation for a polycrystalline catalyst is a comparison of the selectivity of the (100) catalyst with that found for a polycrystalline one as a function of temperature. Figure 4 shows this comparison with the present (100) data compared with the previous data of Anderson and Baker [13] on polycrystalline nickel films. The comparison is a remarkably good one and strongly suggests that the (100) surface is either