

Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen

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FOREWORD

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PREFACE

The petrochemical industries traditionally have depended upon petroleum as their source of feedstocks. The 1973 Arab oil embargo emphasized the need to develop alternate sources. A resultant resurgence of interest in Fischer-Tropsch chemistry will undoubtedly be bolstered by the increased costs and decreased availability now being projected for petroleum supplies.

Work in the field of catalyzed hydrogenation of carbon monoxide began some forty years ago. At reasonably low temperatures, the non-selective production of many organic compounds from carbon monoxide and hydrogen is thermodynamically feasible. It is this nonselectivity that is the major barrier to applying this type of synthesis to our petrochemical needs. Recent research focuses on the development of new catalyst systems that maximize more desirable products (i.e., low-molecular-weight olefins and alcohols).

Thorough investigations of these important reactions are now possible, using improved analytical techniques. Slight variations in reaction conditions have been found to effect significant changes in product selectivity. Small, judiciously placed additions of salts, alkali, or even sulfur (once believed to be detrimental in even trace amounts) to the metal catalyst can enhance product selectivity. Supported metal catalysts have greater stability than unsupported, and the nature of the support material also affects the reaction.

Investigations into these topics are presented in this volume. Iron, nickel, copper, cobalt, and rhodium are among the metals studied as Fischer-Tropsch catalysts; results are reported over several alloys as well as single-crystal and doped metals. Ruthenium zeolites and even meteoritic iron have been used to catalyze carbon monoxide hydrogenation, and these findings are also included. One chapter discusses the prediction of product distribution using a computer to simulate Fischer-Tropsch chain growth.

June 29, 1979

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Kinetics of CO Hydrogenation on Nickel(100)

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A specially designed ultrahigh vacuum system has been used to examine the effect of surface chemical composition on the kinetics of the catalytic methanation reaction. Surface cleanliness is characterized using Auger Electron Spectroscopy (AES) in an ultrahigh vacuum chamber, and reaction kinetics are determined following an in vacuo transfer of the sample to a catalytic reactor contiguous to the AES chamber. Kinetics of CO hydrogenation ($H_2:CO$ ratio of 4:1 and 120 Torr total pressure) over a Ni(100) surface at 450–700 K are compared with those data reported for polycrystalline nickel and high-area-supported nickel catalysts. Very good agreement is observed between both the specific rates and activation energies measured for high-area-supported catalysts and the single crystal Ni(100) surface.

In recent years ultrahigh vacuum methods have been applied to catalytic studies on initially clean metal surfaces having low surface area. In several instances (the hydrogenolysis of cyclopropane over platinum (1) and the catalytic methanation reaction over rhodium (2) and nickel (3)) a link between ultrahigh vacuum methods and conventional catalytic measurements was established. That is, specific reaction rates over low area ($\sim 1\text{--}10\text{ cm}^2$) catalyst samples agreed with specific reaction rates for high area samples ($\sim 100\text{ m}^2/\text{g}$). These data suggest that low area, well-characterized samples can be used as models for working catalysts in studies of catalytic reaction mechanisms, as well as in studies of the mechanism of catalyst deactivation and poisoning.

In the present work, we are using a specially-designed ultrahigh vacuum system to examine the effect of surface structure and surface chemical composition on the kinetics of the energy-related catalytic methanation reaction ($3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$). The catalyst sample is a high-purity single crystal of nickel whose surface is cut to expose (100) planes. The surface cleanliness is characterized using Auger Electron Spectroscopy (AES) in an ultrahigh vacuum chamber, and reaction kinetics are determined following an in vacuo transfer of the sample to a catalytic reactor contiguous to the AES chamber.

In this account of work in progress, we report that the kinetics of CH_4 production over initially clean Ni(100) are in excellent agreement with previous data for polycrystalline nickel foil and high-area-supported nickel catalysts. Traces of surface impurities such as iron act as poisons, causing a marked lowering of the reaction rate.

Experimental

The ultrahigh vacuum apparatus being used for these studies is illustrated in Figure 1. The single-crystal Ni(100) catalyst sample is spot-welded to two short nickel wires and is heated resistively. The sample is mounted on a retraction bellows and can be translated horizontally to various positions. In position 1 the surface chemical composition is determined using electron-excited AES; in position 2 the front and back of the crystal can be dosed with catalyst poisons or promoters using a molecular-beam dosing array. Both positions 1 and 2 are in the ultrahigh-vacuum analysis and surface-preparation chamber. In position 3 the catalyst is located in a high-pressure ($P \leq 1$ atm) stirred-flow catalytic reactor.

The high-purity reactant gases are admitted to the reactor as a 4:1 H_2 :CO mixture at a total pressure of 120 Torr. The product CH_4 is detected using a gas chromatograph calibrated with a standard mixture. The specific reaction rate at a given catalyst temperature and gas pressure is the turnover number (4), N_{CH_4} (number of CH_4 molecules produced per site per second). N_{CH_4} was determined by an absolute measure of the amount of CH_4 produced during a fixed time (typically 2000 sec) at catalyst temperatures ranging from 450 to 700 K; the Ni(100) atom density (1.62×10^{15} atoms/cm²) was used for the number of sites per square centimeter.

Prior to each measurement of catalytic reaction rate, the Ni(100) surface was cleaned using an oxidation-reduction cycle. Figure 2a is an AES spectrum of the Ni(100) crystal after heating; a large impurity sulfur peak is evident. After heating in oxygen at 1×10^{-6} Torr at ~ 1400 K, the sulfur disappears but the surface remains oxygen covered (Figure 2b). After heating in hydrogen at 5 Torr at ~ 800 K for several minutes, followed by heating in vacuum, the clean AES spectrum of Figure 2c results. This is the starting point for all of the kinetic measurements. An AES spectrum from the nickel catalyst after the termination of a reaction rate measurement at ~ 700 K is shown in Figure 2d. A small amount

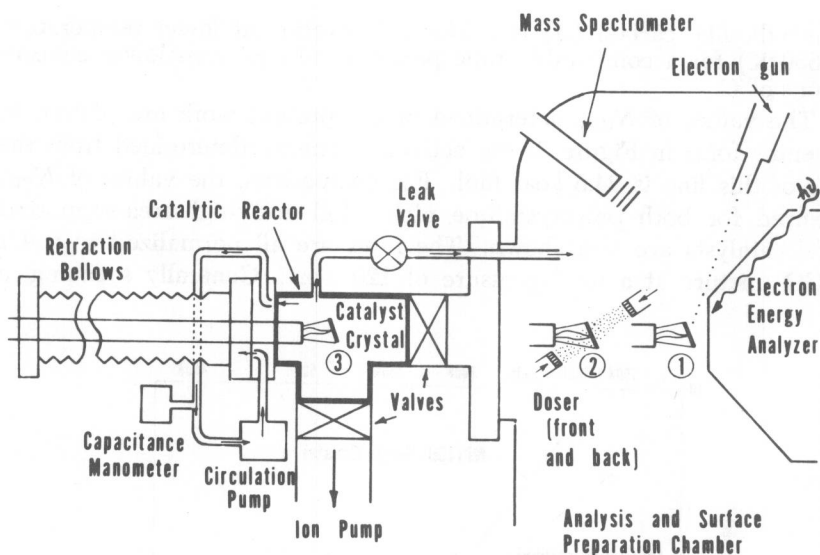


Figure 1. Ultrahigh vacuum apparatus for studying single-crystal catalysts before and after operation at high pressure in catalytic reactor. Position 1: crystal is in position for Auger-electron-spectroscopy study of surface composition, or for UV photoemission spectrum of surface species. Position 2: crystal is in position for deposition of a known coverage of poisons or promoters for a study of their influence on the rate of a catalytic reaction. Position 3: crystal is in position for a study of catalytic reaction rate at elevated pressures, up to 1 atm. Gas at high pressure may be circulated using pump; mass spectrometric/gas chromatographic analysis of the reactants/products is carried out by sampling the catalytic chamber.

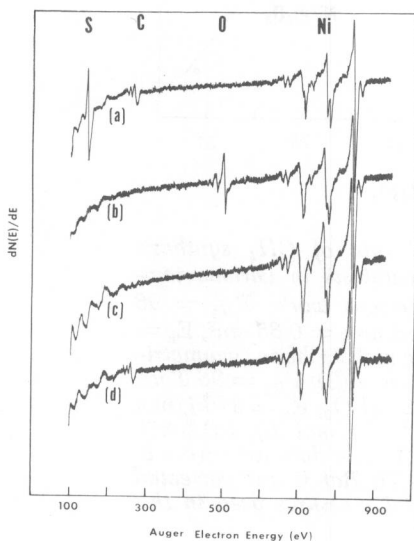


Figure 2. Auger electron spectra of the Ni(100) catalyst sample under different conditions. (a) AES following repeated heating in vacuum to ~ 1400 K. Impurity sulfur (~ 150 eV) and carbon (~ 270 eV) are evident, in addition to the dominant nickel peaks (650–850 eV). (b) AES after heating to ~ 1400 K in oxygen at 1×10^{-6} Torr. Impurity carbon and sulfur are absent, and surface oxygen is present (~ 510 eV). (c) AES after heating surface of (b) at ~ 800 K in hydrogen at 5 Torr. Impurity sulfur, carbon, and oxygen are absent. The broad peaks in the range 100 to 300 eV are believed to be diffraction features (7). (d) AES following methanation reaction in high pressure chamber (4:1 H_2 :CO; $P_{total} = 120$ Torr; catalyst temperature ~ 700 K; reaction run for 2000 sec).

of carbidic-like carbon (5) is evident. Operation at lower temperature (~ 550 K) for a comparable time period results in even lower concentrations of C.

The values of N_{CH_4} determined in the present work are plotted in Arrhenius form in Figure 3; the activation energy determined from the slope of this line is 24.6 kcal/mol. For comparison, the values of N_{CH_4} measured for both polycrystalline nickel foil and high-area-supported nickel catalysts are also shown. The rates are all normalized to a 4:1 H_2 :CO mixture at a total pressure of 120 Torr. Generally speaking, a

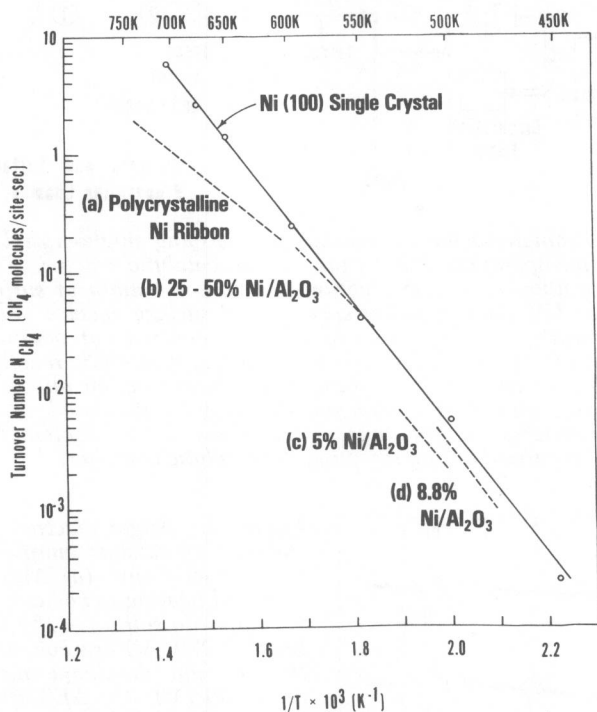


Figure 3. Arrhenius plot of rate of CH_4 synthesis (N_{CH_4}) over different nickel catalysts in various temperature regimes. Ni(100)—present work. $P_{\text{H}_2} = 96$ Torr, $P_{\text{CO}} = 24$ Torr (geometrical area = 0.85 cm^2 , $E_a = 103 \text{ kJ/mol}$). (a) Polycrystalline nickel ribbon (geometrical area = 10 cm^2 , $E_a = 66 \text{ kJ/mol}$ (3)) $P_{\text{H}_2} = 96$ Torr, $P_{\text{CO}} = 24$ Torr. (b) 25–50% $\text{Ni}/\text{Al}_2\text{O}_3$, $E_a = 84 \text{ kJ/mol}$ (8). (c) 5% $\text{Ni}/\text{Al}_2\text{O}_3$, $E_a = 105 \text{ kJ/mol}$ (6). (d) 8.8% $\text{Ni}/\text{Al}_2\text{O}_3$, $E_a = 109 \text{ kJ/mol}$ (6). The data for curves b, c, and d were taken from Table 7b, Ref. 6, and corrected to the hydrogen and CO partial pressures used in this work.

factor of two or three variation in the comparison of turnover numbers is considered good agreement, considering the errors in measurements of reaction rates and active surface area. Thus, there is excellent agreement between both the turnover numbers and activation energies measured for high-area-supported catalysts and single-crystal Ni(100) surfaces. The comparison between values of N_{CH_4} measured on low-surface-area and high-surface-area nickel catalyst samples, as well as the variation in activation energy in Figure 3, have been discussed previously (3). Through the use of the present apparatus, experiments are currently underway on Ni(111) and polycrystalline nickel to investigate the possibility of methanation activity variations on different nickel facets as suggested by the lower turnover numbers measured for the nickel foil compared with the Ni(100) catalyst. It should be pointed out that these earlier data for the polycrystalline nickel were taken in a different apparatus which did not have surface analysis capability.

In several early experiments, severe deactivation of the catalyst sample was observed. AES revealed that large quantities of graphitic-like carbon were present on the deactivated surface, along with small quantities (\sim few tenths of a monolayer) of iron impurity. Qualitatively, it was observed that the carbon and iron scaled with one another. The iron was apparently attributable to traces of impurity iron carbonyls in the reactant CO gas which were efficiently scavenged by the heated nickel catalyst. Storage of the CO over a 1-N₂ cooled trap resulted in an iron-free nickel surface following reaction (cf. Figure 2d). In experiments involving kinetic measurements for periods as long as 10⁵ sec and total product yield less than 1%, no evidence for self-poisoning and no change from the initial rate was observed.

Conclusions: Future Directions

The present results clearly suggest that well-characterized single-crystal samples can serve as models of practical, working catalysts. The ultrahigh vacuum apparatus described herein will be used further to study the pressure dependence of reaction kinetics, and in particular, the systematics of catalyst poisoning in a quantitative fashion (using the molecular beam doser in conjunction with AES).

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Literature Cited

1. Kahn, D. R., Petersen, E. E., Somorjai, G. A., *J. Catal.* (1974) **34**, 294.
2. Sexton, B. A., Somorjai, G. A., *J. Catal.* (1977) **46**, 167.
3. Kelley, R. D., Revesz, K., Madey, T. E., Yates, J. T., Jr., *Appl. Surf. Sci.* (1978) **1**, 266.
4. Madey, T. E., Yates, J. T., Jr., Sandstrom, D. R., Voorhoeve, R. J. H., "Treatise on Solid State Chemistry," N. B. Hannay, Ed., Vol. 6B, p. 1, Plenum, New York, 1976.
5. McCarty, J. G., Madix, R. J., *J. Catal.* (1977) **48**, 422.
6. Vannice, M. A., *Catal. Rev.* (1976) **14**, 153.
7. Becker, G. E., Hagstrum, H. D., *J. Vac. Sci. Technol.* (1974) **11**, 284.
8. Bousquet, J. L., Teichner, S. J., *Bull. Soc. Chim. Fr.* (1969) 2963.

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Hydrocarbon Synthesis Using Catalysts Formed by Intermetallic Compound Decomposition

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Transformed rare earth and actinide intermetallic compounds are shown to be very active as catalysts for the synthesis of hydrocarbons from CO_2 and hydrogen. Transformed LaNi_5 and ThNi_5 are the most active of the materials studied; they have a turnover number for CH_4 formation of 2.7 and $4.7 \times 10^{-3} \text{ sec}^{-1}$ at 205°C , respectively, compared with $\sim 1 \times 10^{-3} \text{ sec}^{-1}$ for commercial silica-supported nickel catalysts. Nickel intermetallics and CeFe_2 show high selectivity for CH_4 formation. ThFe_5 shows substantial formation of C_2H_6 (15%) as well as CH_4 . The catalysts are transformed extensively during the experiment into transition metal supported on rare earth or actinide oxide. Those mixtures are much more active than supported catalysts formed by conventional wet chemical means.

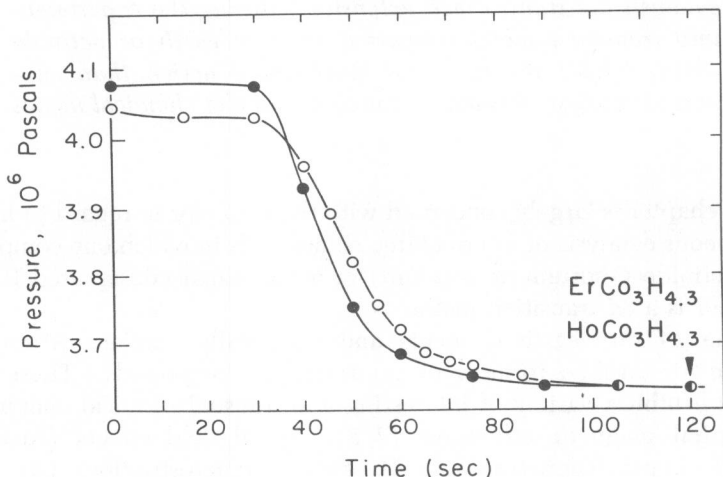
This chapter is largely concerned with the behavior in regard to heterogeneous catalysis of intermetallic compounds in which one component is an actinide (thorium or uranium) or a rare earth (designated R) and the other is a 3d transition metal.

The 14 rare earth elements and chemically similar yttrium and thorium are prolific formers of intermetallic compounds. These compounds exhibit a variety of interesting and unusual physical characteristics—spiral magnetic structures (1, 2), crystal field effects (including Van Vleck paramagnetism) (3, 4), giant magnetostrictions (5), giant magnetocrystalline anisotropies (6), etc. Structural, magnetic, and thermal properties of these materials have been collated and summarized in a recent monography by Wallace (7).

Along with attracting interest from a fundamental point of view, the rare earth intermetallics in recent years have begun to attract widespread attention because of the technological implications of some of their observed physical and chemical properties. They are highly regarded as new materials for the production of high energy magnets and as hydrogen storage media. Both of these are of very considerable significance in regard to the national energy issue.

The solvent power of rare earth intermetallics, specifically LaNi_5 , was first demonstrated by Neumann (8) and shortly thereafter by Van Vucht, Kijpers, and Bruning (9). The latter investigators found that hydrogen is absorbed rapidly and reversibly at room temperature. This feature of the rare earth intermetallics is exemplified (10) for ErCo_3 and HoCo_3 in Figure 1. In the experiment summarized by these plots a container pressurized with hydrogen is brought in contact with the intermetallic. It is noted that pressure drops after a few seconds because of hydrogen absorption by the metal, and the solid reaches a saturation concentration in less than two minutes.

Neutron diffraction studies of hydrogenated rare earth intermetallics show (11, 12, 13) that hydrogen is present in the lattice as a monatomic species. This establishes that hydrogen is absorbed dissociatively. The existence of monatomic hydrogen at the surface, if only fleetingly, suggested that this class of alloys warranted attention as hydrogenation catalysts.



American Institute of Physics

Figure 1. Absorption of hydrogen by bulk specimens of HoCo_3 and ErCo_3 . (●) HoCo_3 , (○) ErCo_3 .

As is indicated in greater detail below, studies have shown that the intermetallics undergo extensive (perhaps total) decomposition in the course of the reactions that are being investigated, and it is highly probable that it is the decomposition products or the transformed intermetallics which are the active catalysts. Initially, the materials were examined as synthetic ammonia catalysts (14). More recently, attention has been directed toward their use as catalysts for the synthesis of hydrocarbons from CO and CO₂.

LaNi₅ is the classic example of a rare earth intermetallic with a large capacity for hydrogen. In view of the considerations set forth above, it was one of the earliest numbers of this class of compounds selected for study. Coon et al. (15, 16) observed that reaction of CO and H₂ over LaNi₅ and its decomposition products and the other RNi₅ compounds as well began at ~ 200°C, and by 380°C 90% of CO was converted in a single pass through the catalyst. Work on the RNi₅ class of compounds is reported elsewhere (15, 16, 17, 18). More recently attention has turned to intermetallic compounds containing manganese and iron. These studies are summarized in the present chapter, along with some newer results obtained using ThNi₅, which appeared in the earlier study to be transformed in the reaction to a substance having unusual activity as a catalyst.

Experimental

The general experimental techniques used have been described in earlier publications from this laboratory (15, 16, 17, 18). However, some important modifications have been instituted recently. The reactions were carried out in a fixed bed, single pass differential reactor. Provisions were made to measure in situ the surface area of the fresh and used catalyst. In the previous studies, argon areas were measured by the Nelson-Eggertsen pulse technique (19). In the course of the work it was established, as noted above, that a material such as ThNi₅ was extensively or totally transformed into ThO₂ and Ni (*vide infra*). It seemed highly probable that the nickel in this instance was the site of the reaction and accordingly there was a need to obtain information about the metallic surface area, or more specifically, the number of active sites, rather than total surface area as is measured with argon absorption. Consequently, chemisorption of CO on the used catalyst also is being measured now. This is accomplished using the pulse technique described by Gruber (20) and Freel (21). In the present work, helium is used as the carrier gas and CO is used for chemisorption. Since impurities in the rather large amount of carrier gas used, compared with the amount of pulsing gas used, can lead to complications, scrupulous attention was paid to the purity of the helium utilized. The carrier gas of the needed purity was obtained as the evaporate from liquid helium. This proved to be necessary to obtain reproducible chemisorption results.

Pretreatment of samples is traditionally an important aspect of catalytic studies. It is of very minor importance for the materials used

in the present work. There appear to be two reasons for this: (1) as is indicated in the following section, the sample is very extensively transformed during the course of the reaction so that pretreatment effects are very rapidly obliterated, and (2) these materials appear to have rather remarkable self-cleaning features, as has been brought out by the very recent UPS work of Siegmann, Schlappbach, and Brundle (22).

Results

Activity of Decomposed ThNi₅. The catalysts formed using the RNi₅ series studied earlier by Coon et al. showed specific activities (based on argon surface areas) larger by one order of magnitude than that of commercial nickel-supported catalysts. The newly obtained chemisorption results lead to the turnover numbers given in Table I. Results for commercially available silica supported nickel catalysts are given for purpose of comparison along with results obtained for transformed LaNi₅ and MmNi₅ (Mm represents mischmetal). The exceptional activity of transformed ThNi₅ and RNi₅ compounds is evident.

As has been alluded to above, the catalysts are extensively transformed when exposed to a mixture of CO and H₂ at $T > \sim 225^\circ\text{C}$. This transformation was first noted by Takeshita, Wallace, and Craig (14) in the use of these materials as synthetic ammonia catalysts. RCo_x and RFe_x intermetallics were converted into iron or cobalt rare earth nitride. This was established by conventional x-ray diffraction measurements. Coon (16) observed that the RNi₅ compounds were transformed by the CO/H₂ mixture into R₂O₃ and Ni, and a similar transformation also was observed by Elattar et al. (17) for ThNi₅, UNi₅, and ZrNi₅. SEM and EDAX results on ThNi₅ show the formation of nickel nodules $\sim 0.5\ \mu\text{m}$ in diameter situated on a ThO₂ substrate.

From the comments in the preceding paragraph it superficially appears that the work to date consists merely in producing supported catalysts in a new way. The conventional way of producing catalysts involves initially wet chemical procedures followed by a calcination proc-

Table I. Turnover Numbers (N) Measured at 205°C

	$10^3 N\ \text{sec}^{-1}$	Ref.
Ni on SiO ₂	1.1 ^a	23
Ni on SiO ₂	0.5 to 1 ^a	24
MmNi ₅	3 ^b	25
LaNi ₅	2.7 ^b	This work
ThNi ₅	4.7 ^{b,c}	This work

^a Based on hydrogen chemisorption.

^b Based on CO chemisorption.

^c $E_{\text{act}} = 80.3 \pm 0.5\ \text{kJ/mol}$.