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AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS-GAS CATALYSTS. FINAL REPORT

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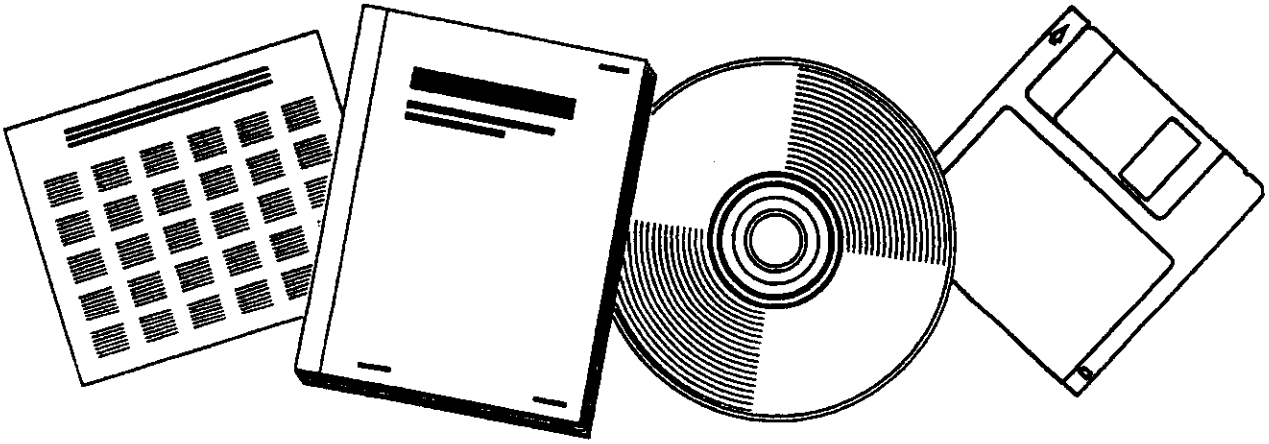

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AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS-GAS CATALYSTS

Final Report

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I. Abstract

This long-term (7.5 year) project has focussed on supported-metal catalysts commonly used in synthesis gas ($CO + H_2$) conversions. These catalysts are very susceptible to sulfur poisoning, and the causes of sulfur deactivation were determined employing surface science and reactor engineering techniques. Transition metal catalysts were synthesized and studied by electron, x-ray, and infrared spectroscopies, and flow reactor systems, with the goal of finding high activity/selectivity systems with sulfur-resistant properties; this effort met with moderate success, but a more worthwhile approach proved to involve the regeneration of working catalysts. Most recently, this research has been concerned with carbon deposition and deactivation of common industrial Co and Ni methanation catalysts, and much insight into the catalytic CO/H_2 conversion process has been attained.

II. Research Objectives

This project combined surface spectroscopy and chemical engineering to investigate five facets of supported-metal catalysts.

1) Determine the rate and extent of sulfur and carbon poisoning of synthesis gas (CO + H_2) conversion catalysts.

2) Synthesize sulfur-tolerant catalysts with high activity and selectivity.

3) Define the kinetics and mechanism of sulfur removal from supported-metal catalysts.

4) Devise regeneration techniques for on-stream catalysts.

5) Examine the role of carbon deposition on a working catalyst.

Auger electron (AES), x-ray photoelectron (XPS), and extended x-ray absorption fine structure (EXAFS) spectroscopies were used to evaluate metal foil and corresponding catalyst surfaces, quadrupole mass spectrometry (QMS) was employed to monitor the syngas conversion products, and infrared spectroscopy and flow reactors were utilized to determine CO bonding and hydrogenation rates as a test of catalyst effectiveness.

III. Research Description and Results

A. Overview, 1975-1979

In order to effectively study deactivation of metal catalysts, a hierarchy of materials was examined; Ni, Co, Fe, and Ru, all effective syngas catalysts, were scrutinized. The early work dealt with bulk metal (i.e., metal foil), so that a set of spectroscopic and reaction standards could be established (References: Windawi - Appendix VII.B.1-4; Windawi and Katzer - App. VII.B.5-7). More conventional catalyst samples were prepared by vacuum deposition of the metal onto the support (typically SiO_2 or α-Al_2O_3), impregnation from metal salt solutions, or metal precipitation (egg shell catalysts). The presence of as little as 10 ppb H_2S in the syngas feed reduced the catalytic activity of all four metals by two or three orders of magnitude (see Figure III.C.1), but Ru was the most resistant. Carbon deactivation of catalysts was noted most strongly when a stoichiometric excess of CO ($H_2/CO<3$) was present in the feed; this poisoning affected activity in the order Fe ≈ Co > Ni ≈ Ru.

Syngas conversions by the metals in this work yield primarily (~90%) CH_4 in the temperature-pressure ranges employed (see III.B), thus allowing the methanation reaction to be a catalyst deactivation barometer. Supported Ru was 20 times as resistant to sulfur poisoning, in keeping with the free energy of surface sulfide formation: i.e., bulk sulfides were in general less stable than surface sulfides, but were more nearly equivalent with Ru. Therefore, higher concentrations of sulfur were necessary to provide Ru with a monolayer cover. With respect to carbon deactivation, both Ni and Ru were only slowly poisoned (reaction conditions: 400°C, 4% CO in H_2), but Co and Fe (see

Figures III.C.2 and III.C.3) were readily deactivated and carbon buildup was extensive. Steady-state methanation activity under these conditions was in the order Ni > Ru > Fe ≈ Co.

Auger and reaction studies of deactivated catalysts were extended to include SO_2-poisoned NO_x reduction systems. Al_2O_3-supported metals (Pt, Pd, Ru, Ni) were deactivated by the formation of extremely stable surface sulfide in a reducing atmosphere; oxidizing environment, however, led to SO_3 and some metal sulfate formation. Reactants were introduced into the feed stream (initially $NO-H_2-NH_3$); relative activities are presented in Table III.C.8. Metal activity was determined as roughly the inverse of catalyst subsurface oxygen concentration, and O_2 in the feed largely eliminated SO_2-poisoning (Reference: Tsai _et al_ - App. VII.B.8).

Kinetic and mechanistic studies of CO hydrogenation and sulfur removal were completed with the use of flow reactors and AES/QMS, respectively. At low CO partial pressures, Ni, C- and S-poisoned Co, and S-poisoned Ru had syngas conversion dependent on $[CO]^y$ while untreated Co and Ru were dependent as $1/[CO]^z$ (y and z non-integer). Sulfur removal was monitored by AES (Reference: Windawi and Katzer - App VII.B.9), using Ni as a model system; subsequent QMS data reduction revealed that sulfur loss was a function of O_2 partial pressure, sample temperature, and sulfur content. This reactivation method was developed into a patent covering six hydrogenation-active transition metals: 1-10 ppm O_2 in an inert gas, passed over S-poisoned catalysts at 300-500°C, would completely regenerate the activity. Carbon deposition had no effect on this process (Reference: Windawi and Katzer - App. VII.B.10).

The inclusion of CO_2 or O_2 in the feedstream was examined as a potential antidote to sulfur poisoning, but no significant improvement in the rate of deactivation was found. Apparently these molecules did not remain chemisorbed long enough to react with the adsorbed sulfur.

Some effort was directed at metals supported by oxides capable of very strong catalyst interactions; again, Ni was employed as a model system. Supports such as TiO_2 and ZrO_2, which exhibit strong metal-support interactions, cause the CO/H_2 product distribution to change significantly. These supports were more resistant to S-poisoning than conventional γ-Al_2O_3 (see Figure III.C.4), but activities were not as great. Preparative methods also play a role: Ni/TiO_2 impregnation catalysts generated the greatest amounts of high molecular weight hydrocarbons (C_2 - C_7) of any system tested (see Figure III.C.5).

B. Summary, 1980-1982

Methanation Studies:

The catalytic CO hydrogenation properties of Co on α-Al_2O_3 were examined, with special attention paid to carbon and sulfur poisoning. Sulfur-free reactions were carried out at 200-400°C and 1 atmosphere pressure of 0.1-20% CO in H_2 in a metal-free quartz reactor (see Figure III.C.6). Data reduction revealed two pseudo-steady states, an active state with a methanation turnover number (MTN) of 15 ± 5 sec^{-1} and a passive state with MTN ≈ 0.1 sec^{-1}. Auger spectra revealed that the surface of the active catalyst consisted of reaction intermediates on Co, while the passive (or deactivated) realm featured massive graphite carbon deposits. The ratio of methane to higher products was 9:1; higher CO concentrations led to low turnover rates (Reference: Agrawal et al - App. VII.B.11).

Sulfur deactivation of Co/α-Al_2O_3 was studied with 13-100 ppb H_2S in 1-4% CO/H_2 at 390°C; relative methanation activities (vs. S-free conditions) were 10^{-3} at 13 ppb H_2S and 10^{-4} at 90 ppb. The presence of surface sulfide was determined by AES, and complete coverage was noted at the lowest H_2S concentration; no bulk (sub-surface) sulfide as detected, however. Sulfur deactivation was a result of geometric site blockage, with one adsorbed S for two surface Co atoms; carbon deactivation played only a minor part in this catalyst poisoning (Reference: Agrawal et al -App. VII.B.12).

Very similar studies were carried out on a Ru/α-Al_2O_3 system at 250-400°C, 0.1-4% CO in H_2, and H_2S levels from 0-100 ppb. Up to 10% C_2 species were detected in the product stream at lower temperatures, but only CH_4 was found at 400°; increases in CO concentration suppressed CH_4 formation. Auger studies revealed no graphitic surface or bulk carbon, nor was there any sub-surface sulfide in H_2S experiments. As above, S-deactivated catalysts had one S atom blocking two metals; 13 ppb H_2S lowered activity by a factor of 50 at 400°. The strongly reducing atmosphere mitigated the S-tolerance of Ru (Reference: Agrawal et al -App. VII.B.13).

Finally, Ni/γ-Al_2O_3 was examined for sulfur resistance in methanation reactions at 388°C with 13-100 ppb H_2S in 4% CO/H_2. The steady-state methanation activity dropped by a factor of 200 with the introduction of 13 ppb H_2S and fell 5000-fold at 100 ppb levels. Poisoning was again attributed to site blockage (see Figure III.C.7); surface nickel sulfides were found to be 15 kcal/mole more stable than bulk Ni_2S_3 (Reference: Fitzharris et al - App. VII.B.14).

Infrared Studies:

The greatest obstacle in sulfur deactivation studies is the requirement of a metal-free environment. Thus, it was necessary to construct an infrared cell capable of withstanding elevated temperatures and reduced pressures, but with the sample compartment readily accessible to the operator. The successful design incorporated an all-quartz body and sample holder with NaCl windows imbedded in commercial screw-on vacuum adaptors with Viton O-ring seals. These cells have been operated continuously for several hours at 550°C and 10^{-6} torr without failure. Repeated temperature-pressure cycling to atmospheric conditions has not proven harmful (Reference: Moon et al - App. VII.B.15).

This cell was first applied in a vibrational (and electron) spectroscopic study of carbon-deactivated Ni and Co catalysts. The reactor studies performed earlier had shown that the activation energy for $Co/\gamma-Al_2O_3$ dropped from 28 to 16 kcal/mole upon carbon deactivation, whereas Ni catalysts exhibited an activation energy of 24 kcal/mole for both the fresh and used samples. All the obvious causes for this change in activation energy on Co, such as diffusion limitation, were eliminated, leading to the conclusion that an electronic effect of the deposited carbon gave rise to the energy change observed. The use of CO as a probe of the electronic environment of a surface is well known, since its vibrational frequencies are modified according to its bonding to surface atoms. Fourier transform infrared (FTIR) was employed to follow the adsorption of CO; first as a function of CO pressure and second as a function of carbon deposition. On Ni/γ-Al_2O_3, it was possible to follow CO bonding from three-fold sites to linear M-CO as the gas pressure is increased; on Co/γ-Al_2O_3 only the linearly bonded species was observed, irrespective of CO pressure.. Carbon deposition was accomplished by heating the catalysts in CO, and AES revealed that the carbon was carbidic at 250°C heating, but graphitic with 400° temperatures. Surface carbon formations were monitored by the changes in CO vibrational frequencies; these shifts were consistent with CO absorption on single Ni atoms, in preference to bridged sites, and indicated that Co-C bonds were stronger than Ni-C bonds (Reference: Moon <u>etal</u>- App. VII.B.16).

Studies of carbon monoxide adsorption by FTIR were extended to sulfur-poisoned Ni and Co on γ-Al_2O_3. After room-temperature CO adsorption, nickel-CO vibrational signals appeared at 2053 cm^{-1} (M-CO) and 1949 cm^{-1} $(\mathrm{M}{\diagup}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{M})$, while Co-CO moieties had two bands (2044 and 2028 cm^{-1}) arising from non-identical linear species. As the surface is sulfided (by H_2S/H_2 = 1 at 550°C and 10^{-6} torr), the lower frequency bands with both metals disappeared, and the remaining bands shifted to higher frequency. This implied that sulfur has a preference for the higher energy (i.e., more stable) M-CO sites, and while sulfur poisoning reduced the number of available sites, the residual surface carbonyls were more weakly adsorbed by the metal. As in earlier work, AES studies revealed only surface metal sulfide (Reference: S. Bahl - M.Ch.E. thesis).

Since Co was shown to be a more suitable CO hydrogenation catalyst than Ni, a more detailed infrared study of Co/γ-Al_2O_3 was undertaken, looking in particular at the effects of metal loading; catalysts were prepared with

5 wt% and 12 wt% Co. Carbon monoxide adsorption was a function of the amount of Co metal present; the lower loading catalyst had IR signals consistent with reduced Co-CO and a weak, vacuum-sensitive Co oxide-CO band, while the 12% Co gave no sign of the oxide. An XRD study indicated Co particle sizes of 29Å and 36Å for the 5 and 12 wt% samples, respectively. It was proposed that the larger clusters have a greater percentage of surface Co, and are thus easier to reduce. Consistent with earlier studies, carbon deposition caused vibrational frequencies to increase ca. 50 cm^{-1} (Reference: Onuferko _et al_ preprint - III.D.1).

Carbon Deposition and Deactivation:

Carbonaceous residues on Co and Ni foils have been examined by AES and XPS to determine the nature and extent of the deposited materials. Carbon deposition occurred in a CO atmosphere (0.1-10 torr) at 400°C over timed exposure intervals. Both metals showed surface carbide formation at low pressures and short CO exposure periods; increased pressure and exposure times, up to 30 min. at 10 torr, created graphitic carbon on both Co and Ni. More severe exposure conditions of 4 hr at 400°C and 10 torr revealed a major difference between the carbon forms deposited on the two metals. Argon ion sputtering studies yielded the information that on Ni, ca.6Å of graphitic carbon had formed over the surface carbide, whereas on Co, a graphitic deposit of ca.9Å covered an 18Å carbidic layer. The formation of this bulk Co carbide provides an explanation of the observed drop in activation energy for CO versus Ni in syngas conversion reactions (Reference: Onuferko and Katzer preprint - III.D.2).

Extended x-ray absorption fine structure (EXAFS) spectroscopy was used to examine carbon deposition on 12 wt% Co/γ-Al_2O_3 catalysts. Following H_2 reduction, the samples had metal crystallites of 36Å (XRD) with a Co-Co distance of 2.5Å (EXAFS); the latter figure was consistent with cubic Co. After sample exposure to 1 atmosphere of CO at 400°C, EXAFS spectra were Fourier transformed to reveal strong peaks in the radial distribution function at 1.85Å and 2.92Å, corresponding to Co-C (1.83Å) and Co-Co (2.89Å) distances in Co_2C. This supports earlier AES/XPS work on this system (Reference: Khalid _et al_ preprint - III.D.3).

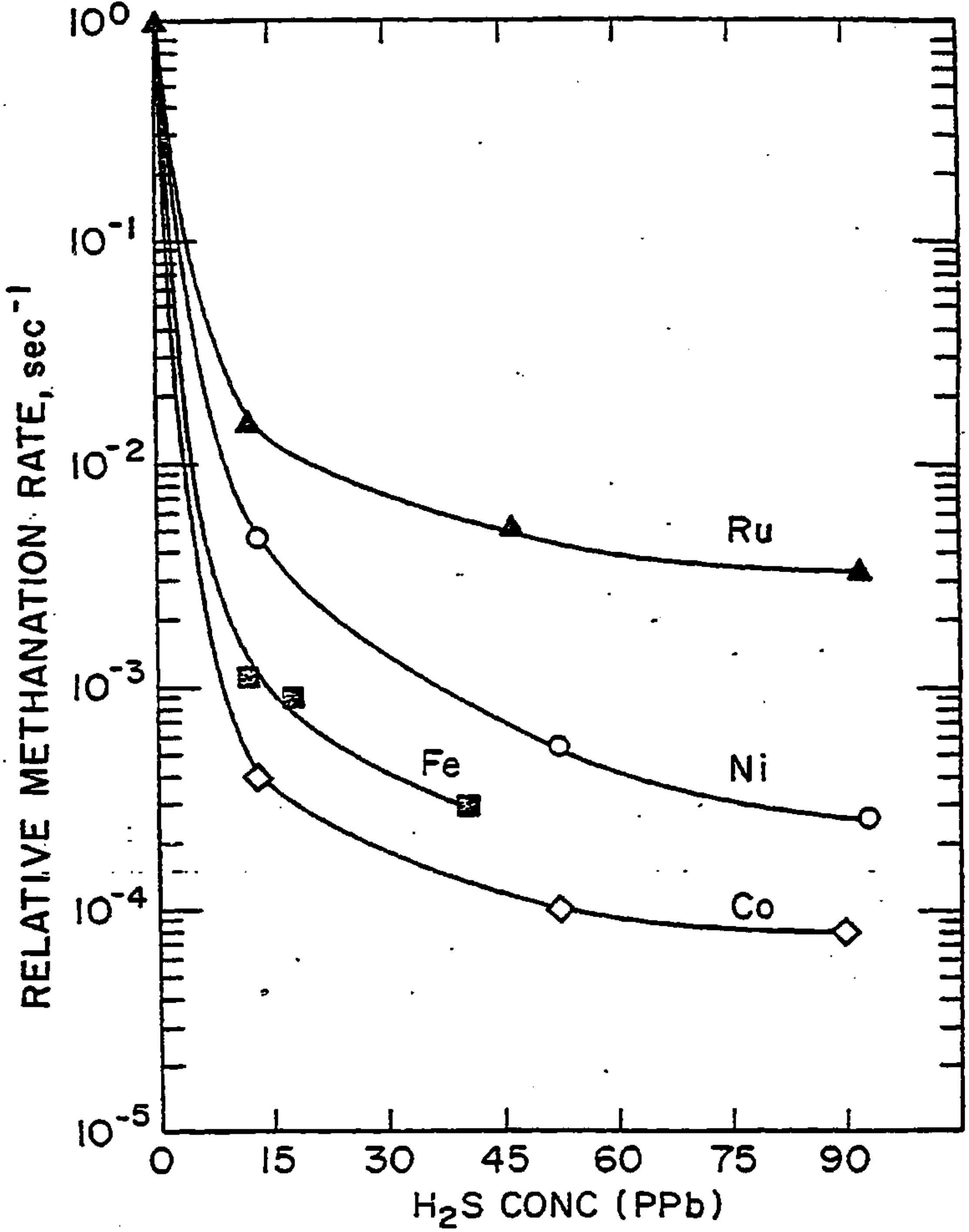


Fig. III.C.1. A comparison of transition-metal methanation catalysts (Ni, Co, Fe, and Ru) in their sensitivity to poisoning by H_2S in gas phase at 390°C. The methanation rate presented here is relative to the fresh catalyst activity of the metal. In the case of Ni/Al_2O_3, 4% CO/H_2 was used, in other cases 1% CO/H_2 was used.

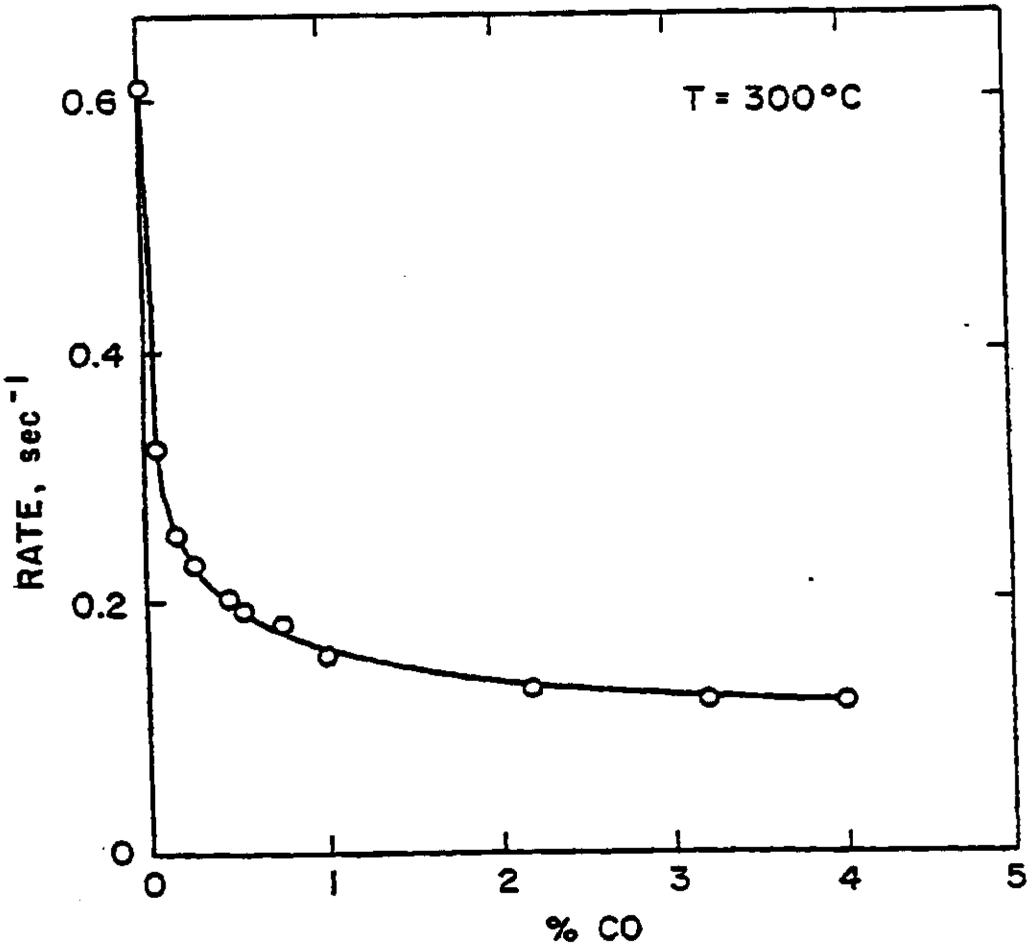


Fig. III.C.2. Methanation activity of Co/Al_2O_3 as a function of P_{CO} at 300°C in the upper steady-state region.

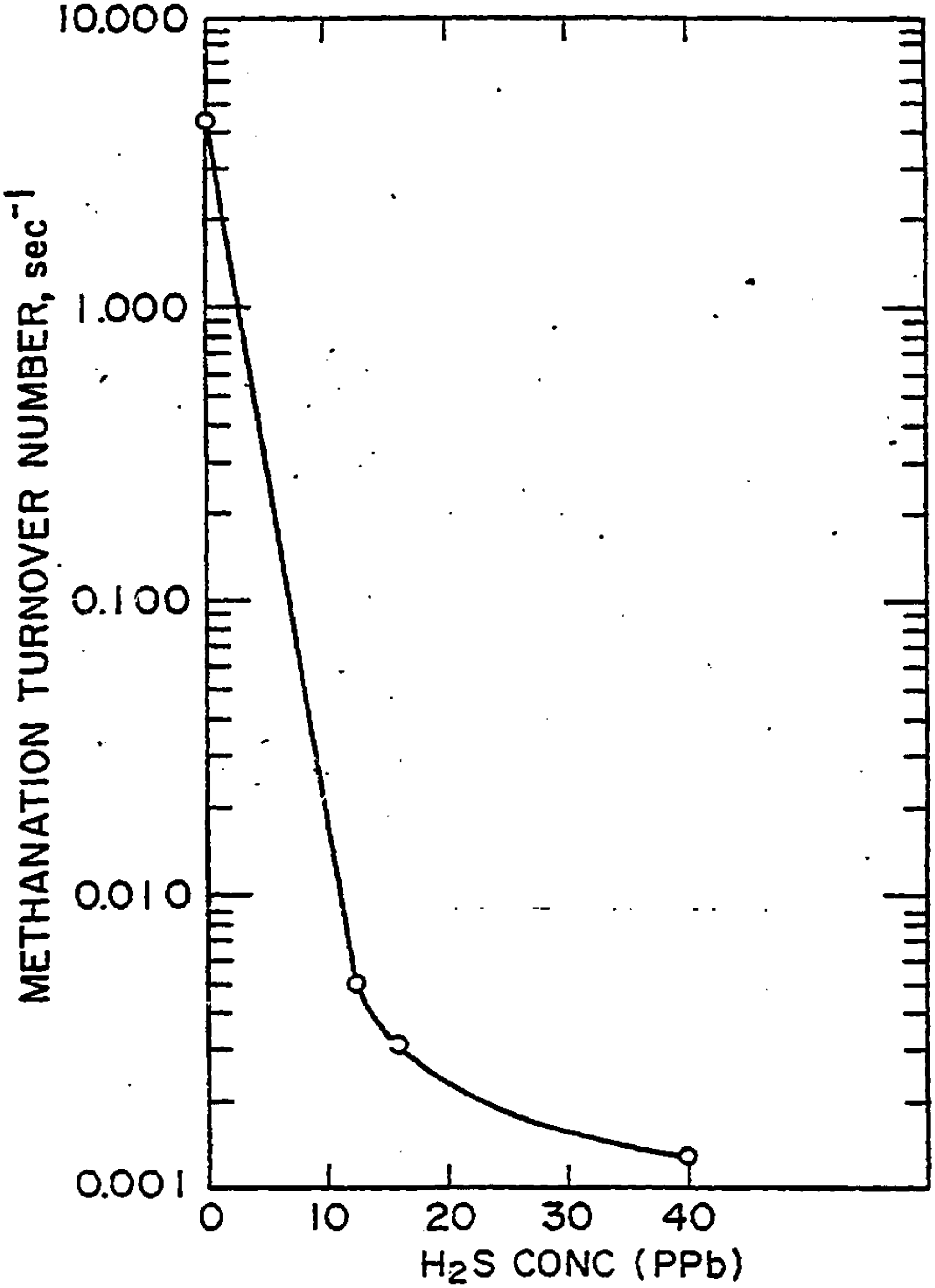


Fig. III.C.3. Methanation activity of Fe/Al$_2$O$_3$ as a function of H$_2$S concentration at 390°C, 1% CO/H$_2$.

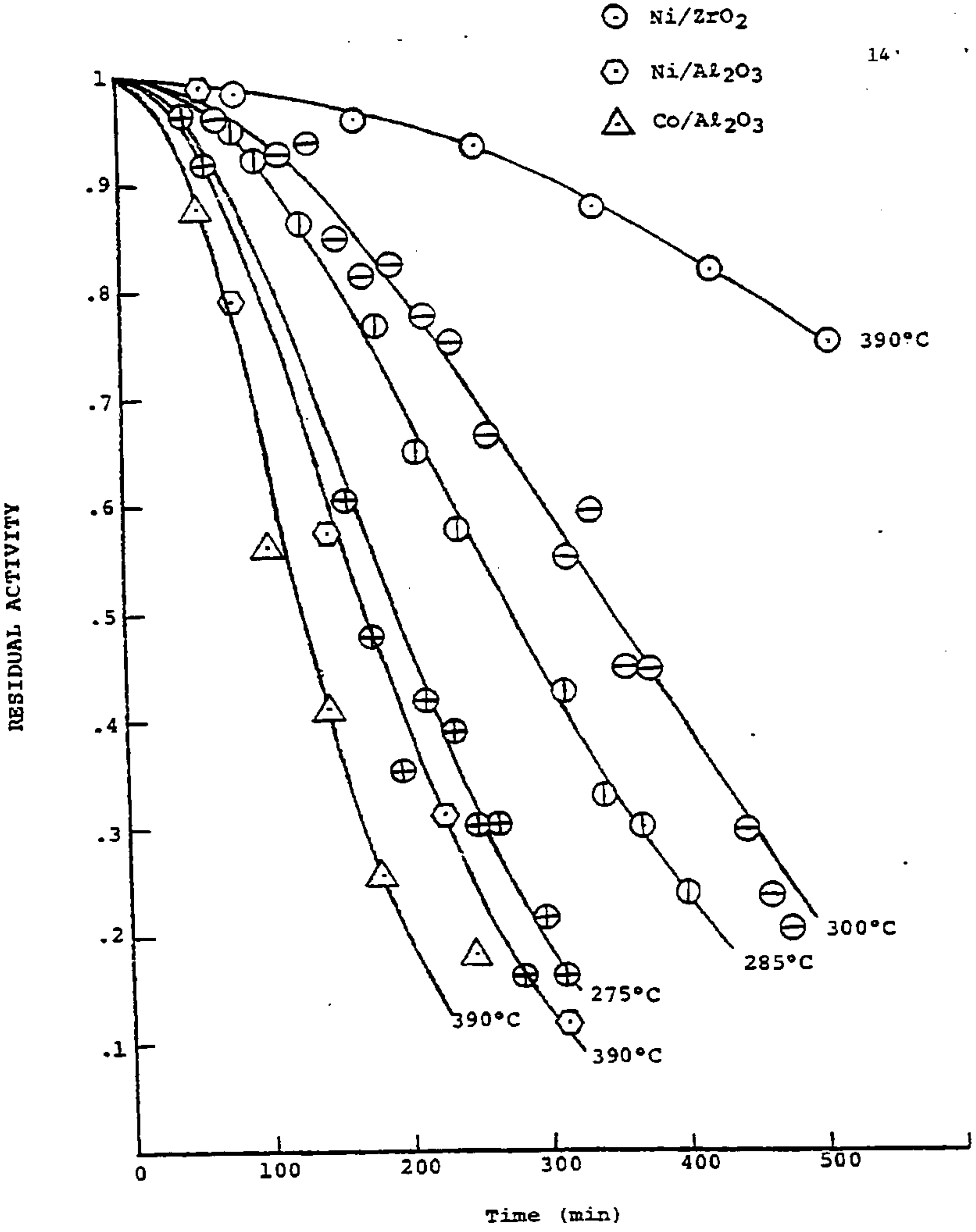
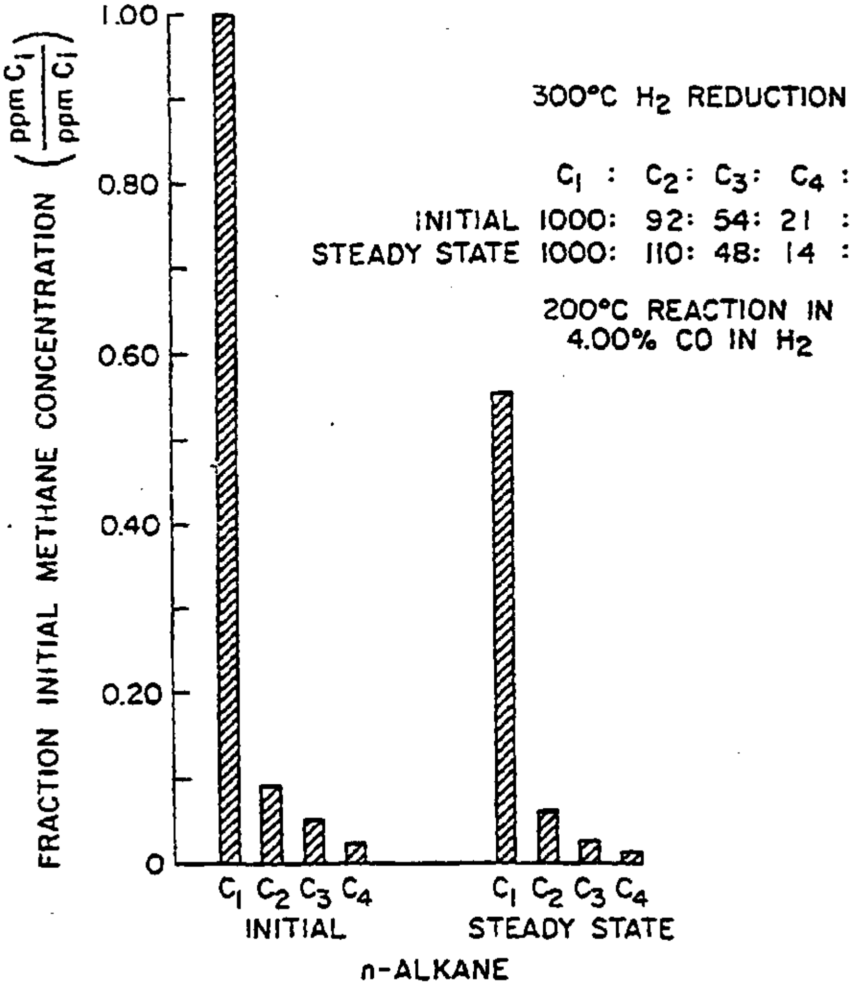
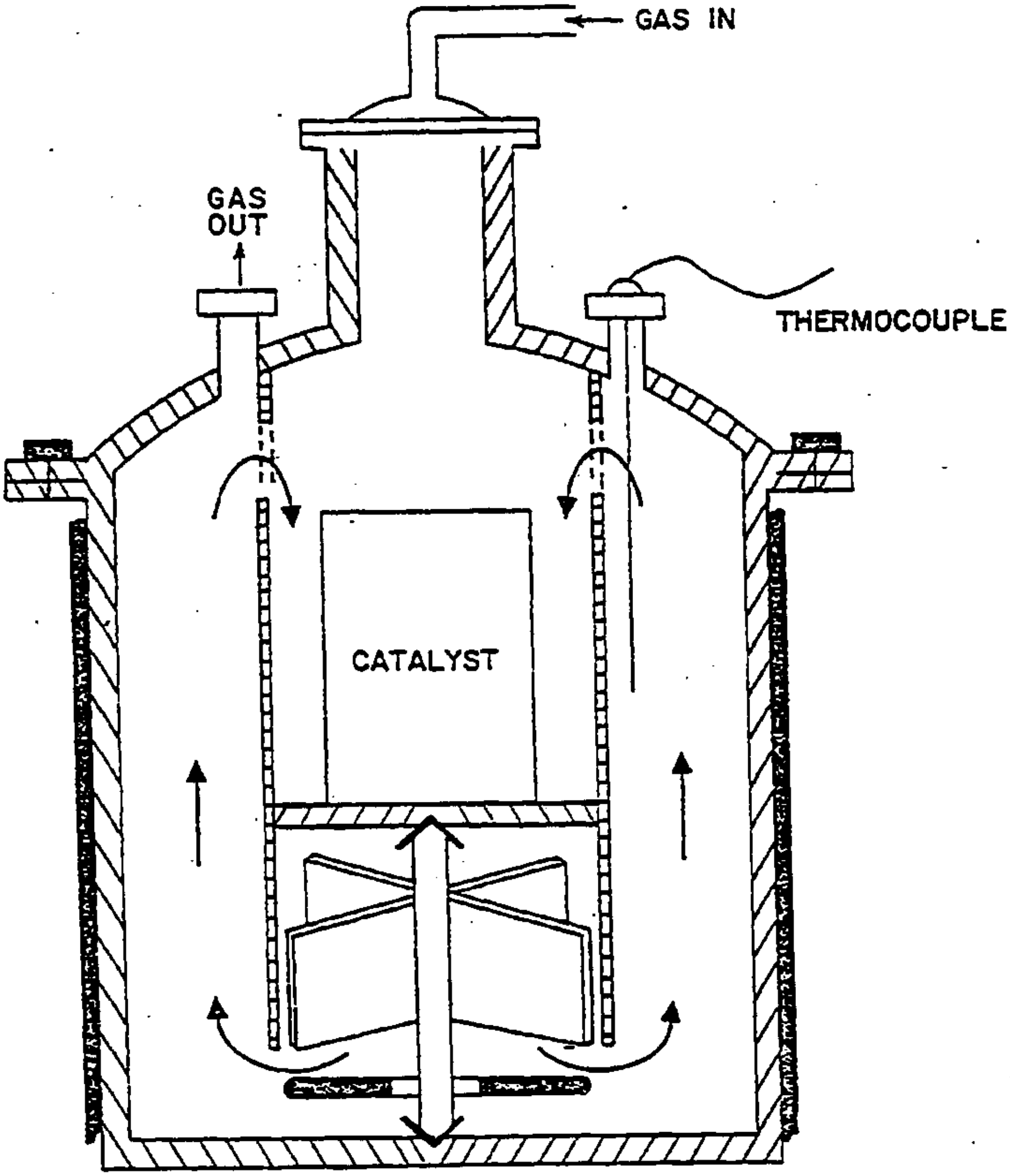


Fig. III.C.4. Time dependence of the methanation activity of catalysts poisoned *in situ* with H_2S concentrations of; 5 ppm: Ni/ZrO_2 at 275°C, 285°C, and 300°C, 55 ppb: Ni/ZrO_2, Ni/Al_2O_3, and Co/Al_2O_3 at 390°C. The 390°C data were obtained from studies made on shell or "thin film" catalysts, while the remainder were from studies made on pellets.



INITIAL vs STEADY STATE SELECTIVITY FOR Ni ON TiO_2 IMPREGNATED (2.01% Ni)

FIG. III.C.5.



SCHEMATIC OF MAGNETICALLY-DRIVEN INTERNAL RECYCLE REACTOR

Fig. III.C.6.

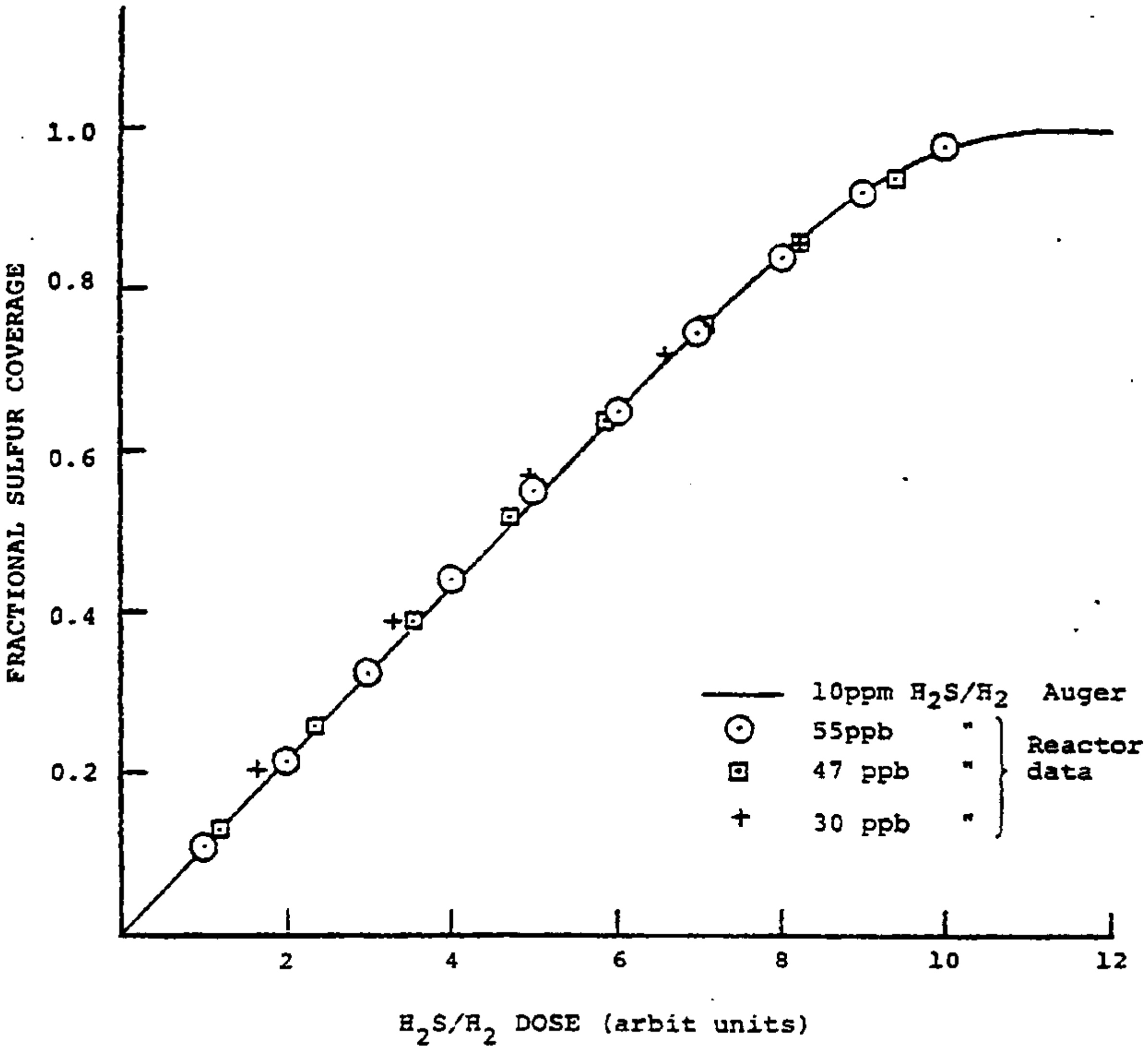


Fig. III.C.7. Development of the fractional coverage of sulfur on nickel with dosing by H_2S/H_2. Reactor data (dosing during CO hydrogenation) are normalized to Auger data (molecular leak system).

Table III.C.8

Metal activity in NO_x reducing catalysts:
The effects of oxidizing and reducing environments.

Feed Stream Components	Relative Catalytic Activity
$NO-H_2-NH_3$	Pt ≈ Pd > > Ru > Ni
$NO-H_2-NH_3-O_2$	Pt > > Pd > Ru ≈ Ni
$NO-H_2-NH_3-SO_2$	Ru > > > Pt ≈ Pd ≈ Ni
$NO-H_2-NH_3-O_2-SO_2$	Pt > > Pd > Ru > Ni

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