

are, on the other hand, larger than in romeriids.

In addition to these modifications of the skull, *Petrolacosaurus* is advanced over the romeriid stage in a series of postcranial features. Many of these advanced features are seen in the Late Permian eosuchians *Youngina*, *Heleosaurus* (9), *Galesphyrus*, and *Kenyasaurus* (10) and even in Triassic thecodonts and squamates. Seven elongated vertebrae form a long neck; these vertebrae have anteriorly inclined centrosphenes and prominent median ventral keels. Posterior cervical and anterior dorsal vertebrae have well-developed mammillary processes on the sides of the neural spines. The vertebrae from the midcaudal region are also elongate. Some cervical ribs have anterodorsally directed processes near the tubercula. The scapulacoracoid is lightly built. The pelvic girdle, on the other hand, is very massive. The humerus is long and slender, in contrast to the robust femur. Distal limb elements are elongate, slender, and equal in length to the proximal limb elements. The carpus has elongate proximal elements, and the tarsus has an incipient mesotarsal joint, a locked tibioastragalar joint, a single centrale, and a widely divergent fifth metatarsal. The ribs, long bones, and metapodials are hollow.

The large number of highly significant similarities through the skeletons of *Petrolacosaurus* and various eosuchians justify inclusion of this genus within the order Eosuchia. These similarities are not restricted to the advanced features discussed above. Primitive morphological characters seen in the diapsids named above are clearly inherited from a common ancestor, the romeriids. These primitive features, although of little value in establishing phylogenetic relationships, indicate that *Petrolacosaurus* is primitive enough to have given rise to later eosuchians. Certain advanced features of eosuchians, such as cranial modifications toward development of a middle ear system sensitive to airborne sound (11), are lacking in *Petrolacosaurus*, necessitating placement of this genus within a separate family, Petrolacosauridae, at the base of the Eosuchia.

Acceptance of *Petrolacosaurus* as an ancestral eosuchian indicates a long hiatus in the fossil record of the eosuchian radiation between the first evidence in the Upper Pennsylvanian and the subsequent differentiation in the Late Permian. The extent of the Early Triassic diapsid radiation confirms that the origin of the eosuchians should be sought much earlier, probably well within the Paleozoic close to the origin of all reptiles, as *Petrolacosaurus* appears to sub-

stantiate, but the intervening gap is puzzling. The conditions of preservation and the nature of the fossils at Garnett suggest that *Petrolacosaurus* and other terrestrial tetrapods, invertebrates, and plants were washed into a quiet lagoon from dry ground. The gap in the fossil record can, therefore, be partially explained by the assumption that the early diapsids lived in environmental conditions which were not under normal circumstances conducive to preservation—areas away from standing water.

Recent studies of all the known diapsid species from the Upper Permian and Lower Triassic of south and central Africa (12) show that this stage of the diapsid evolution is far more complicated and extensive than was formerly believed. A more complete picture of the early diapsid adaptive radiation is required in order to understand fully how *Petrolacosaurus* is related to later diapsids. It can, however, be stated that the general anatomy of *Petrolacosaurus* and other early eosuchians indicates that they are certainly much closer to the more advanced diapsids and provide a better link with the ancestral romeriids than any other group of Palaeozoic reptiles.

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conclusions and place *Petrolacosaurus* in a total of five different suborders within three reptilian subclasses. In 1953 and 1954 Peabody collected more specimens, but he died before he could undertake a reconsideration of the anatomy of *Petrolacosaurus*. His collection forms the basis of the present study with well-preserved adult specimens partially articulated in such critical areas as temporal region and palate (specimens KUMNH 9951, 9952, 33602, and 33603).

2. All living reptiles can be grouped into four orders: Chelonia, Rhynchocephalia, Squamata, and Crocodylia. The latter three can be associated with the largest assemblage of fossil reptiles, collectively called the diapsids. The diapsid condition refers to the presence of two pairs of temporal openings on the skull roof behind the orbit. This condition has been retained in a primitive pattern in the crocodylians and the sole living rhynchocephalian *Sphenodon* but has been modified in the squamates by progressive loss of the dermal bones in the temporal region.
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  11. The middle ear in romeriids and *Petrolacosaurus* could not function as in most advanced eosuchians and modern reptiles, as a highly sensitive mechanical transformer that amplified small sound pressures impinging on a large, taut tympanum into strong pressures at the small fenestra ovalis. The area behind the skull could not accommodate a large tympanum because the muscle depressor mandibularis hugged the convex posterior edge of the skull. The stapes was very massive and extended to the quadrate bone. A large stapes, immovable by normal sound pressures, would be ideal, however, in transmitting tissue-conducted sounds through the large footplate to the inner ear. It is relatively easy to derive the structural conditions seen in eosuchians and other diapsids from that in romeriids or *Petrolacosaurus* [R. R. Reisz, thesis, McGill University (1975)].
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  13. I thank T. H. Eaton, Jr., of the University of Kansas who suggested this study and lent me the specimens of *Petrolacosaurus*.
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## Intermetallic Compounds of the Type $MNi_5$ as Methanation Catalysts

**Abstract.** *Catalytic reactions of carbon monoxide with hydrogen have been studied in which intermetallic compounds of the formula  $MNi_5$  (where M is thorium, uranium, or zirconium) have been used as the catalysts. The materials perform effectively as methanation catalysts;  $ThNi_5$  has a specific activity exceeding that of a typical commercial oxide-supported methanation catalyst by a factor of about 5. This material also shows superior resistance to hydrogen sulfide poisoning. Nickel, formed as a decomposition product of the  $MNi_5$  intermetallic compound, is probably the active species, but its properties are influenced by the nature of M in the precursor  $MNi_5$  system.*

We have studied intermetallic compounds of the formula  $MNi_5$ , where M is Th, U, or Zr, with respect to their activity as catalysts in the formation of hydrocarbons (primarily  $CH_4$ ) from CO and  $H_2$ .

These materials are a part of a class of compounds represented by the formula  $MT_5$  [where T is Co or Ni, and M is a rare earth ( $RNi_5$ ), an actinide, or a group IVa element], which are noteworthy as hy-

Table 1. Characteristics of several Ni-containing methanation catalysts.

Catalyst*	Decomposition product	Sample weight (g)	Sample area (m <sup>2</sup> )	Surface area per mass (m <sup>2</sup> /g)	Saturation temperature† (°C)	CH <sub>4</sub> ‡ (moles per 100 moles)	CO <sub>2</sub> (moles per 100 moles)	C <sub>2</sub> H <sub>6</sub> content	H <sub>2</sub> S‡§ (cm <sup>3</sup> )
"ThNi <sub>5</sub> "	Ni/ThO <sub>2</sub>	0.5012	9.0	18	≥291	7.2 (209)	0.1	Small amount	78 (291)
"UNi <sub>5</sub> "	Ni/UO <sub>2</sub>	0.2020	6.1	30	≥367	0.7 (218)	0.03	Trace	25 (288)
"ZrNi <sub>5</sub> "	Ni/ZrO <sub>2</sub>	0.5199	14.6	28	≥362	0.7 (206)	0.004	Trace	10 (356)
Harshaw Ni		0.1630	20.4	125	≥291	3.6 (217)	0.006	Small amount	40 (285)

\*Quotes signify that the enclosed is the precursor to the actual catalyst. †At the saturation temperature only insignificant amounts of CO remain unreacted. ‡The number in parentheses is the experimental temperature (in degrees Celsius). §The volume of H<sub>2</sub>S at standard temperature and pressure needed to completely deactivate the catalyst.

drogen absorbers (1). Since the hydrogen is absorbed dissociatively (2), it must be present on the surface, at least fleetingly, as a monatomic species. For this reason it appeared that the MT<sub>5</sub> compounds might be effective hydrogenation catalysts. This expectation has been borne out in recent work involving the synthesis of NH<sub>3</sub> from the elements (3) and in the reaction of CO + H<sub>2</sub> to form CH<sub>4</sub> (4). In our earlier experiments the intermetallic compounds investigated were of the type RNi<sub>5</sub>. In the work reported here we have considered MNi<sub>5</sub> intermetallics in which M represents a non-rare-earth element.

The reaction of CO + H<sub>2</sub> over ThNi<sub>5</sub>, UNi<sub>5</sub>, or ZrNi<sub>5</sub> was studied in a flow reactor. The molar ratio of H<sub>2</sub> to CO was 3:1. The quantities of catalyst used varied between 0.2 and 0.5 g. The space velocity was about 6700 hour<sup>-1</sup>, which is sufficiently high to avoid limitation by diffusion. The activities of the MNi<sub>5</sub> samples (or of the decomposition products of these intermetallics) were compared at ~200°C, where the conversion is small. At this temperature the reaction is in the kinetic region, and heat and mass transfer effects are negligible. (At higher temperatures the conversion of CO is essentially complete and hence it is not possible to compare relative catalytic effectiveness.)

We analyzed the gas mixture emerging from the reactor with a gas chromatograph. Surface areas were measured in situ by the continuous flow method of Nelsen and Eggertsen (5). We carried out this measurement using a mixture of N<sub>2</sub> and He gases (25 moles of N<sub>2</sub> per 100 moles of the gas mixture).

The activities of the intermetallics are indicated in Table 1. Results for Harshaw Ni-0104T are included for comparison. X-ray diffraction studies of these non-rare-earth MNi<sub>5</sub> catalysts showed, as was the case for our earlier studies of RNi<sub>5</sub> catalysts, extensive decomposition into Ni and the oxide of the partner metal. As a result of our studies of RNi<sub>5</sub> catalysts we believed that the active species was Ni supported on the rare-earth oxide (4); however, the activity varied considerably among the catalysts studied. This is also

true of the MNi<sub>5</sub> intermetallics studied in the present investigation. We believe that the difference is a consequence of variations in the Ni surface or of specific interactions between the metal and the supporting oxide, or both.

We also studied the sensitivity of the catalysts to poisoning by H<sub>2</sub>S by injecting small volumes of H<sub>2</sub>S gas into the reaction mixture in steps and noting the decline in catalyst activity. The quantities of H<sub>2</sub>S needed to poison the catalysts completely are given in Table 1. Dalla Betta *et al.* studied H<sub>2</sub>S poisoning for several Ni methanation catalysts and observed (6) that a continuous feed of H<sub>2</sub>S (10 parts per million) was sufficient to significantly lower their steady-state activities. The steady-state activity of the unpoisoned catalyst is in the order Raney Ni > Ni/Al<sub>2</sub>O<sub>3</sub> > Ni/ZrO<sub>2</sub> (where Ni/Al<sub>2</sub>O<sub>3</sub> represents Ni supported on alumina), but this order reverses after poisoning. As indicated in Table 1, "ZrNi<sub>5</sub>" is much more susceptible to H<sub>2</sub>S poisoning than the other compounds, and "ThNi<sub>5</sub>" is relatively resistant to H<sub>2</sub>S. Thus the nature of the element with which Ni is combined in the precursor intermetallic compound is also important.

Although the surface area of the catalyst produced from ThNi<sub>5</sub> is relatively low, its activity as a methanation catalyst is the highest of the four systems studied. Its specific activity in yield per square meter of surface area exceeds that of the commercially available methanation catalyst (Harshaw Ni-0104T) by a factor of about 5.

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## Mercury Emissions from Geothermal Power Plants

**Abstract.** *Geothermal steam used for power production contains significant quantities of volatile mercury. Much of this mercury escapes to the atmosphere as elemental mercury vapor in cooling tower exhausts. Mercury emissions from geothermal power plants, on a per megawatt (electric) basis, are comparable to releases from coal-fired power plants.*

Recent reports (1-4) have expressed concern about the potential toxicity hazards and environmental contamination of mercury emissions from geothermal areas in Hawaii, New Zealand, and Iceland. Indeed, mercury has been shown to be associated in elevated concentrations in a wide variety of natural thermal fluids (5-8). Natural mercury contamination of the marine environment during volcanic activity has also been reported (9), and other studies of mercury

distributions in the oceans and their sediments strongly suggest that large quantities of mercury enter the oceans from submarine volcanic activity (10-13).

Because of this potential for mercury mobilization, a research program was initiated to study mercury emissions from existing geothermal power plants. We present here our initial findings of the quantities and chemical forms of mercury in emissions from two producing geothermal power developments: the