

Preliminary communication

**CATALYSIS OF THE WATER GAS SHIFT REACTION
BY A $\text{Ru}_3(\text{CO})_{12}$ -2,2'-BIPYRIDINE COMPLEX**

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Summary

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with 2,2'-bipyridine in water under a carbon monoxide atmosphere affords a high activity low-temperature catalyst for the water gas shift reaction.

The water gas shift reaction (WGSR) is catalyzed by metal oxides in industrial applications [1]. Temperatures in the range of 200–550°C are necessary for the reaction to proceed at an acceptable rate. The equilibrium for the reaction is shifted in the direction of the reactants at higher temperatures. The residual carbon monoxide concentration at equilibrium is too high for some applications, e.g. for the ammonia synthesis, even at lower temperatures [1].

We have found that $\text{Ru}_3(\text{CO})_{12}$ and 2,2'-bipyridine form a highly active heterogeneous catalyst, which operates at low temperatures [2]. A systematic study of the iron group trinuclear carbonyl clusters and heterocyclic amines showed most of the $\text{Ru}_3(\text{CO})_{12}$ based systems to be active in the homogeneous WGSR [3,4]. These systems often suffer, however, from low activity or from the occurrence of a reaction between carbon dioxide and the amine which limits the number of the catalytic cycles.

The 2,2'-bipyridine diamine shows behaviour which is different from the other amines. Upon heating it forms a dark blue complex with $\text{Ru}_3(\text{CO})_{12}$, which is adsorbed strongly on glass and silica surfaces. The complexation and formation of the active catalyst is not instantaneous; an induction period of more than 24 h at 100°C and $p(\text{CO})$ 0.5 atm, $p(\text{H}_2\text{O})$ 1.0 atm is necessary to activate the system. The air-sensitive compound thus formed is not soluble in polar or nonpolar solvents.

Table 1 shows the WGSR activities of the activated catalyst as a function of temperature and the initial CO pressure. The catalysis was studied in a glass vessel

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TABLE 1

 $\text{Ru}_3(\text{CO})_{12}$ -2,2'-BIPYRIDINE AS A CATALYST FOR THE WATER GAS SHIFT REACTION ^a

Initial CO pressure (torr)	Temperature (°C)	T.O.F. ^b /24 h	
		H ₂	CO ₂
400	100	690	690
550	100	1100	1100
600	150	4400	4400

^a Conditions: H₂O 0.36 ml; $\text{Ru}_3(\text{CO})_{12}$ 20 μmol ; 2,2'-bipyridine 60 μmol . ^b T.O.F., turnover number = mol of gas evolved per mol of $\text{Ru}_3(\text{CO})_{12}$ charged.

containing water and the catalyst under carbon monoxide. The gas concentrations (CO, H₂ and CO₂) were analyzed before and after the reaction by gas chromatography [3]. The activities are reported for both H₂ and CO₂ production. The values for carbon dioxide show the true catalytic nature of the system. The turnover frequencies depend on the initial CO pressure and on the reaction temperature. The measured catalytic activities are among the highest reported for WGSR under comparable reaction conditions.

Chemical and IR-spectroscopic analysis of the catalyst show the presence of ruthenium carbonyl and 2,2'-bipyridine. A $\text{Ru}_3(\text{CO})_{12}$ -amine molar ratio of 3/1 was found to give the highest activity. A detailed structural analysis has been reported for a related complex, $\text{Ru}_3(\text{CO})_{10}(\text{bipy})$, in which the bipy ligand is coordinated bidentately to a single metal center [5].

The catalytic properties of a ruthenium carbonyl/2,2'-bipyridine mixture in the WGSR have been described earlier [6] for a system that was photo-catalytic and homogeneous. The catalyst was $[\text{RuCl}(\text{CO})(\text{bipy})_2]\text{Cl}$ and the reported activities were an order of magnitude lower than those we observed. Another related study involved the catalytic reduction of nitrobenzene to aniline by a $\text{Ru}_3(\text{CO})_{12}$ -bipyridine system, in which a good conversion was found [7].

In conclusion, bipyridine interacts with metal clusters to give potentially interesting systems which deserve further investigations.

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References

- 1 C.N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980, 292.
- 2 T. Venäläinen, T.A. Pakkanen, T.T. Pakkanen, and E. Iiskola, Finn. Pat. 69620.
- 3 T. Venäläinen, E. Iiskola, J. Pursiainen, T.A. Pakkanen, and T.T. Pakkanen, *J. Mol. Catal.*, 34 (1986) 293.
- 4 T. Venäläinen, E. Iiskola, T.A. Pakkanen, and T.T. Pakkanen, *J. Mol. Catal.*, 34 (1986) 305.
- 5 T. Venäläinen, J. Pursiainen, and T.A. Pakkanen, *J. Chem. Soc. Chem. Commun.*, (1985) 1348.
- 6 D. Choudhury, and D.J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.*, (1982) 1885.
- 7 E. Alessio, G. Clauti, and G. Mestroni, *J. Mol. Catal.*, 29 (1985) 77; E. Alessio, G. Zassinovich, and G. Mestroni, *ibid*, 18 (1983) 113.