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METALCARBIDES: A NEW NO_2-NO CONVERTER MATERIAL FOR A CHEMILUMINESCENT NO_x ANALYZER

Natsuko FUTSUHARA,* Kazue MASUDA,* Koji TSUCHIMOTO,** and Naoomi YAMAKI***

* National Research Institute for Pollution and Resources, Kawaguchi, Saitama 332

** Mitsubishi Oil Company, Kawasaki-ku, Kawasaki 210

*** Department of Environmental Chemistry, Faculty of Engineering, Saitama University, Urawa, Saitama 336

Metalcarbides are investigated as a new NO_2-NO converter material for measuring NO_2 by using a chemiluminescent NO_x analyzer. It is found that the metalcarbides make it possible to convert quantitatively NO_2 to NO under very mild conditions without the oxidation of NH_3 and N-compounds and without the decomposition of NO.

A chemiluminescent method, based on the reaction of ozone with nitric oxide (NO), has been very useful for determination of low NO concentration in the atomosphere.[1) When this device is applied to the measurement of nitrogen dioxide (NO_2), it is necessary to reduce NO_2 to NO quantitatively. For this purpose, a heated carbon, stainless steel, or molybdenum (NO_2-NO) converter has been usually employed in commercial chemiluminescent analyzers. With regard to these converters, however , the following problems in the precise measurements have been pointed out[2-4)]; 1) potential interferences from ammonia (NH_3) and other N-containing compounds, 2) quantitative conversion of NO_2 to NO under a wide concentration range of NO and NO_2, 3) NO decomposition through the converter. In order to solve these problems, various kinds of metalcarbides are investigated as new converter materials which can reduce NO_2 to NO at a very low reaction temperature.

A series of metalcarbides (WC, Mo_2C, Cr_3C_2, TaC, TiC, VC, B_4C, SiC, ZrC, and NbC) were obtained from Toshiba Tungaloy Co. An ($NO+NO_2$) sample gas ranging 0 to 10 ppm concentration were prepared from a pre-calibrated cylinder gas (NO 4 ppm and NO_2 24 ppm in N_2) by diluting with a cylinder air. NO and NO_2 concentration were determined by the chemiluminescent NO_x analyzer equipped with a platinum wire converter at the high temperature of 950°C. (It is accepted that the platinum wire converter converts NO_2 to NO at this temperature.[5]) The efficiency for NO_2 to NO conversion was tested under the following condition;

NO_2	0.6 ppm in air	Total flow rate	2 l/min
NO	0.1 ppm in air	S.V.	20,000 hr^{-1}
Metalcarbide	6 ml	Reaction temperature	100-400°C

The efficiency for NO_2 to NO conversion is difined;

$$\frac{[\text{outlet NO}] - [\text{inlet NO}]}{[\text{inlet } NO_2]} \times 100 \quad (\%)$$

The degree of NH_3 oxidation to NO was calculated according to the equation;

$$[\text{outlet NO}]/[\text{inlet } NH_3] \quad \times 100 \quad (\%)$$

Air balanced NH_3 gas (1.15 ppm) passed through the metalcarbide converter at various temperatures under the same flow conditions mentioned above.

Table 1 shows the values of NO_2 to NO conversion obtained for ten kinds of metalcarbides at various temperatures. All the metalcarbides except ZrC and NbC had very high reactivity even at temperatures lower than 300°C.

Taking into consideration the experimental results concerning the response time for 95% conversion of NO_2 and the thermal stability above 300°C, WC, Mo_2C and TaC were superior to the other metalcarbides as the converter material.

Table 1. Efficiency of NO_2-NO Conversion (%)

Metalcarbide	100°C	200°C	300°C
WC	96	99	99
Mo_2C	96	97	99
Cr_3C_2	93	99	94
TaC	89	97	99
TiC	92	98	99
VC	89	95	99
B_4C	82	94	99
SiC	86	96	99
ZrC	63	81	-*
NbC	0	90	-*

* The metalcarbides burned at the temperature.

The plot of the produced NO vs. the introduced ($NO+NO_2$) concentration (0-10 ppm) for WC in Fig. 1 under the range of reaction temperatures 100-300°C gives a good straight line which passes through the origin and has the slope equal to 45 degree. It is confirmed that the introduced NO_2 is completely changed to NO within a wide range of concentrations without NO decomposition and that the high activity of the metalcarbide at the low temperatures is a significant advancement in the NO_2-NO converter. Similar results were obtained for both Mo_2C and TaC.

Figure 2 shows a relationship between the reaction temperature and the conversion of NH_3 to NO with regard to the three metalcarbides of WC, Mo_2C and TaC. Apparently, NH_3 conversion is negligibly small at temperatures lower than 250°C. Furthermore, when a sample gas including NO_2 and N-containing compounds such as PAN and ethylnitrate passed through the chemiluminescent and UV analyzers,[6] measured NO_2 concentrations agreed well each other at the converter temperature lower than 150°C. It indicates that the N-containing compounds scarcely change to NO through the converter at the conditions.

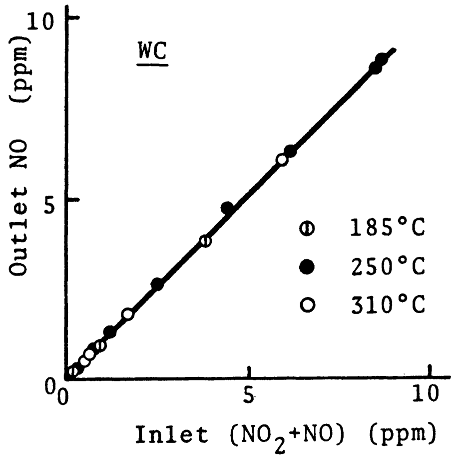

Fig.1. Produced NO vs. Introduced ($NO+NO_2$).

When these converters are applied to ambient samples, it is very important to examine the reactivity of oxygen with the metalcarbides, which causes the fast consumption of the converter materials. Additional experiments have been performed to obtain the reaction rates of metalcarbides (WC, Mo_2C and TaC) with NO_2 and O_2 under the following conditions;

NO_2	280 ppm in helium
O_2	21 % (cylinder air)
Total flow rate	1 l/min
Metalcarbide	0.5 g

The reaction rates were determined from the formation rate of ($CO+CO_2$) in the following reactions by using a Beckman Model 6800 THC-CO-CO_2-CH_4 analyzer.

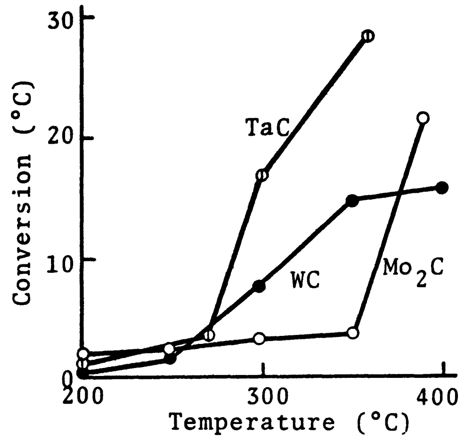

Fig.2. NH_3 Conversion to NO vs. Temperature of Converter.

$$NO_2 + MC \xrightarrow{R_{NO_2}} CO + CO_2 + NO + MO_x \qquad (1)$$

$$O_2 + MC \xrightarrow{R_{O_2}} CO + CO_2 + MO_x \qquad (2)$$

In Table 2, the both reaction rates (R_{NO_2} and R_{O_2}) and the ratios (R_{NO_2}/R_{O_2}) at various temperatures are given for WC, together with the ratios for Mo_2C and Cr_3C_2. The reaction rates of the metalcarbides with NO_2 and O_2 increased with the increase of temperature, especially the former rate depended on temperature more strongly than the latter one and hence became larger than the latter one above 400°C.

Table 2. Reaction Rates of Metalcarbides with NO_2 and O_2, and their Ratios

Reaction Temp. (°C)	Reaction Rate of WC*		R_{NO_2} / R_{O_2} Ratio		
	R_{NO_2}	R_{O_2}	WC	Mo_2C	Cr_3C_2
200	4.2	0.0034	1200	5.7	8.8
250	18	0.059	310	3.9	2.1
300	60	0.99	61	2.9	1.3
350	110	11	10	1.8	0.58
400	140	220	0.64	0.29	0.34

* ($CO+CO_2$) formation rate [ppm/min], referred to equations (1) and (2).

It is apparently found from the ratios of R_{NO_2}/R_{O_2} that the metalcarbides selectively react with NO_2 at the temperature lower than 300°C and were slowly consumed by O_2 in the sample. It is to be noted that the ratios for WC are much larger than those for Mo_2C and Cr_3C_2 under the same conditions.

As a result of the continuous operation of the WC converter at 200°C under the sampling conditions for the TECO-14B NO-NO_x analyzer, it is confirmed that the high initial efficiency remains constant throughout over 3 months.

In conclusion the metalcarbides make it possible to convert quantitatively NO_2 in ambient air to NO under the very mild conditions such as the low reaction temperature, without the oxidation of NH_3 and N-compounds and without the decomposition of NO.

References and Notes

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