

Effects of Microwave Absorbents in NO Removal by Microwave Discharge of NO/Ar Mixture at Atmospheric Pressure

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The removal of NO has been studied using a microwave-absorbent assisted discharge of an NO/Ar mixture at atmospheric pressure. When carbon fibers (CFs) and a graphite rod were used as absorbents, the conversion of NO increased by factors of 31–71%.

Recently much attention has been attracted to removal of NO_x using electric discharges and catalytic-assisted discharge systems.^{1–6} Various types of energy and radiation can be used to generate discharge. Compared with other discharge, microwave discharge is energy efficient because a large amount of energy is converted to the production of energetic electrons rather than into the heating of gases, and the performance is good due to the large discharge region. We have recently applied a microwave discharge to NO removal.^{2,6} NO was decomposed by microwave discharge diluted in a rare gas. Although stable discharge could be operated in the wide total-pressure range of 1–760 Torr (1 Torr = 133 Pa) in NO/Ar mixtures at a microwave power of 200 W, discharge must be initiated at a low pressure below 50 Torr. It was found that about 75% of NO could be decomposed into N₂ and O₂ by microwave discharge of an NO/Ar mixture at NO and Ar flow rates of 25 and 1000 sccm (standard cubic centimeter per minute), respectively, a total pressure of 760 Torr, and a microwave power of 200 W.

In order to initiate discharge at atmospheric pressure and to improve NO conversion, NO removal in an NO/Ar mixture has been studied here by coupling microwave discharge with various microwave absorbents. In addition to graphite, SiC, Cu, BN, Zr, and Co₃O₄, four types of CFs, which have NO reduction abilities, were employed as new microwave absorbents. The decomposition efficiency and discharge products are analyzed using mass spectrometry.

The discharge-flow apparatus used for the study of NO removal was described elsewhere.⁶ It consisted of a quartz discharge tube, a stainless-steel flow tube, and an ULVAC MSQ400 quadrupole mass spectrometer (QMS). The quartz discharge reactor is shown in Figure 1. The discharge-flow apparatus was continuously evacuated using a 0.06 m³ min⁻¹ rotary oil pump. The flow rates of NO and Ar were kept at 25 and 1000 sccm, respectively, and their mixture was fed into a microwave discharge. We used a lower microwave power of 100 W than that of 200 W in the previous work⁶ in order to suppress CO and CO₂ emissions from carbon materials and to reduce microwave heating of absorbents. The total pressure was varied from 1 to 760 Torr by closing a variable gate valve placed between the discharge reaction and the main pump. The mass spectra of discharge products and residual NO were measured

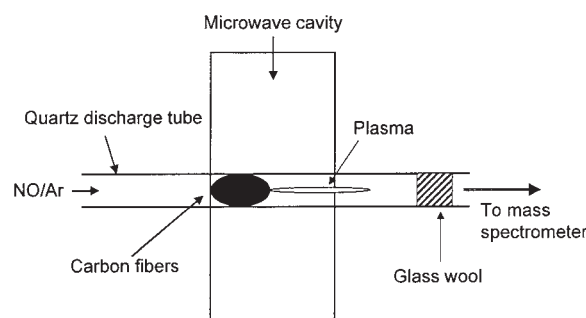


Figure 1. Microwave-absorbent assisted discharge-flow reactor used for NO decomposition.

through sampling orifices using the QMS.

In Table 1 are summarized the results for NO decomposition by microwave discharge over various absorbents. For comparison, the results obtained without using absorbents are also shown. The experimental uncertainties were within 5%. The following ten materials were used as microwave absorbents: isotropic pitch based CF heat-treated at 1200 °C, activated CFs (Osaka Gas OG-10A and 20A) having surface areas of 1000 and 2000 m²/g, respectively, mesophase pitch based CF heat-treated at 1000 °C, graphite rod ($\phi = 5 \times 10$ mm: Nilaco), SiC powder (β type: Kishida Chem. Co.), Cu rod ($\phi = 2 \times 9$ mm: Nilaco), Zr rod ($\phi = 3 \times 15$ mm: Nilaco), BN rod ($\phi = 3 \times 15$ mm: Fur-uuchi Chem.), and Co₃O₄ powder (Kishida Chem. Co.). It is known that Co₃O₄ has high NO decomposition activity itself as well as microwave absorbing ability.⁴

The NO conversion without using any absorbent was 35%. CFs and graphite rod enhanced the NO conversion by factors of 31–71 and 57%, respectively. On the other hand, SiC, Cu, Zr, BN, and Co₃O₄ showed little NO decomposition activity. These results indicated that CFs and graphite rod have high NO decomposition activity in microwave discharge. The decomposition activity of CF OG-20A was higher than that of OG-10A, indicating that the surface area is an important factor to generate decomposition activity from CFs.

For the practical use of microwave discharge, it is necessary to ignite discharge at atmospheric pressure. Discharge could be initiated at atmospheric pressure when CFs and Zr were used. On the other hand, the ignition pressure of discharge must be kept at <50 Torr, when the graphite rod, SiC, Cu, BN, and Co₃O₄ were employed. About 6–18% of carbon fibers was lost during discharge for 15 min due to oxidation. The reduction rate of the graphite rod was smaller than those of CFs by factors of 32–90, though such a large difference was not observed in the NO decomposition activity between the CFs and graphite rod. A small

Table 1. NO decomposition by a microwave discharge of NO/Ar mixture using microwave absorbents^a

Absorbent	Conversion of NO/%	Ratio ^b	[N ₂ + CO]/[NO] ₀ ratio ^c /%	[O ₂]/[NO] ₀ ratio/%	[CO ₂]/[NO] ₀ ratio/%	Reduction of absorbent ^d /%	Ignition pressure of discharge /Torr
Without absorbent	35	1.00	17	18	—	—	<50
Isotropic pitch based CF	52	1.49	27	19	11	8.6	760
Activated CF (OG-10A)	46	1.31	23	17	9.0	13	760
Activated CF (OG-20A)	60	1.71	32	24	13	18	760
Mesophase pitch based CF	56	1.60	30	22	8.5	6.3	760
Graphite rod	55	1.57	28	23	3.3	0.2	<50
SiC	35	1.00	21	18	3.4	0.4	<50
Cu	34	0.97	17	14	—	0.2	<50
Zr	31	0.89	15	14	—	0.0	760
BN	35	1.00	21	18	—	0.1	<50
Co ₃ O ₄	38	1.09	20	17	3.8	0.5	<50

^aNO and Ar flow rates were 25 and 1000 sccm, respectively, a total pressure was 760 Torr, and microwave power was 100 W. ^bConversion ratio of NO to that without using absorbent. ^c[NO]₀ denotes an initial NO concentration before decomposition. ^dDischarge period was 15 min.

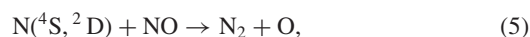
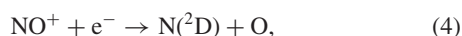
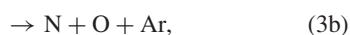
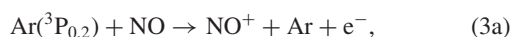
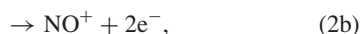
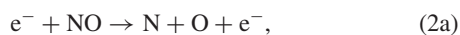
loss was also observed for Co₃O₄ after discharge due to its reduction by discharge.

When CFs and graphite rod were used, the formation of CO₂ was observed as a byproduct. It was difficult to distinguish between N₂ and CO by mass spectrometry. However, the formation ratios of [N₂]/[NO]₀ predicted from the conversion of NO agreed well with those of the observed [N₂ + CO]/[NO]₀ ratio. It was therefore reasonable to assume that the formation ratio of CO was much smaller than those of N₂ and CO₂. It is clear from Table 1 that the graphite rod is the best absorbent except for its low ignition pressure because of a relatively high conversion of NO, and high [N₂ + CO]/[NO]₀ ≈ [N₂]/[NO]₀ and [O₂]/[NO]₀ ratios and a low [CO₂]/[NO]₀ ratio. An advantage of CFs is a high ignition pressure of discharge, while their disadvantage is high [CO₂]/[NO]₀ ratios. It seems that mesophased pitch based CF is best among four CFs studied because of a relatively high conversion of NO, and high [N₂ + CO]/[NO]₀ ≈ [N₂]/[NO]₀ and [O₂]/[NO]₀ ratios and a low [CO₂]/[NO]₀ ratio.

In the previous paper,⁶ we concluded that major active species in microwave discharge of NO/Ar mixtures are energetic electrons and metastable Ar(³P_{0,2}) atoms on the basis of optical spectroscopic and mass spectrometric data. The NO molecules are decomposed into N₂ and O₂ in microwave discharge of NO/Ar mixtures by the reactions of these active species:



Dominant reaction pathways leading to N₂ and O₂ are predicted to be following electron-impact dissociation and ionization (2),⁷ Penning ionization (3a), and dissociation (3b) followed by electron-ion recombination (4),⁸ two-body reactions of N(⁴S, ²D) with NO (5), and three-body recombination (6):



No evidence of the NO₂ formation through the subsequent reactions was observed in the present experiments.

The superior decomposition activity over CFs and graphite rod results from either an increase in electron density of plasma or reduction of NO on carbon surfaces leading to CO₂:



The formation rates of CO₂ from CFs were about 3–4 times higher than that from the graphite rod. These results suggest the contribution of the latter reduction process of NO on carbon surfaces is more significant for CFs due to their larger surface area.

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