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CONVERSION OF Rh(III) SPECIES ON Rh-Y ZEOLITE DURING EXPOSURE TO CARBON MONOXIDE REVEALED BY TPD TECHNIQUE

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On the exposure of fresh Rh-Y zeolite to CO, the formation of the rhodium species responsible for the TPD peak of CO at 473-500 K, which was followed by the conversion into the second type rhodium species responsible for the peak at 563-583 K, was observed.

The oxidation state of the rhodium species on the fresh Rh-Y zeolite has been found to be trivalent.[1-5] It has been suggested that the $Rh(I)(CO)_2$ species are formed by the reaction of the Rh(III) species with CO.[1,5] However, further details on the conversion of Rh(III) species during the exposure to CO have not been clarified. In the present study, on the Rh-Y zeolite exposed to CO, two clearly distinct states of adsorbed CO have been observed by a temperature programmed desorption technique (TPD).

Rh-Y zeolites were prepared from Na-Y zeolite and an aqueous solution of rhodium trichloride trihydrate by stirring the mixture at 353 K for 12 h. After the solid was dried at 393 K overnight, it was pressed, crushed, and then sieved to 20-42 mesh size. The apparatus used was a conventional flow-type reactor. The catalyst (1.0 g), which was placed in the reactor (Pyrex glass tube, 10 mm i.d.), was heated to a desired temperature at the rate of 2 K/min in a He-CO stream (total flow rate = 50 cm^3(STP)/min), and kept at the temperature usually for 5 h, and then cooled to room temperature in a helium stream. The catalyst was then heated at the constant rate of 2 K/min in the helium stream (30 cm^3(STP)/min) up to 723 K. The effluent gas sampled by a syringe was analyzed by gas chromatography to determine the concentration of CO and CO_2 desorbed from the catalyst.

Typical TPD spectra of CO and CO_2 obtained from the fresh Rh-Y zeolite (2.0 wt%) exposed to CO at 393 K are shown in Fig.1. The spectrum clearly showed two peaks; the maxima for the first peak (denoted by A_1) and for the second peak (denoted by A_2) were at 500 K and 573 K, respectively. On a control TPD run on the Na-Y zeolite exposed to CO at 393 K, no appreciable desorption of CO and CO_2 was observed. The agreement in the peak positions of CO_2 with those of CO in the temperature region below 593 K indicates that the formation of CO_2 in this region is due to the secondary reaction of the desorbed CO.

Further TPD results are summarized in Table 1. The majority of the rhodium species formed by the exposure to CO at 353 K corresponds to the species for the peak A_1(the peak position was at 473 K). On the Rh-Y zeolite with the adsorption at 433 K, however, the peak A_2 was predominant. A longer duration for the exposure resulted in a higher ratio of A_2/A_1. And then, the ratio of A_2/A_1 in run 2 with the adsorption at the CO concentration of 30% is lower than that in run 5 at the CO concentration of 10%. The amounts of ($CO+CO_2$) were found to be almost the same in the desorption runs on the Rh-Y zeolite(2.0 wt%). This suggests that the rhodium species responsible for A_2 are formed by the conversion of the rhodium species responsible for A_1. This conversion was accelerated at a higher temperature, while a higher CO pressure retarded it.

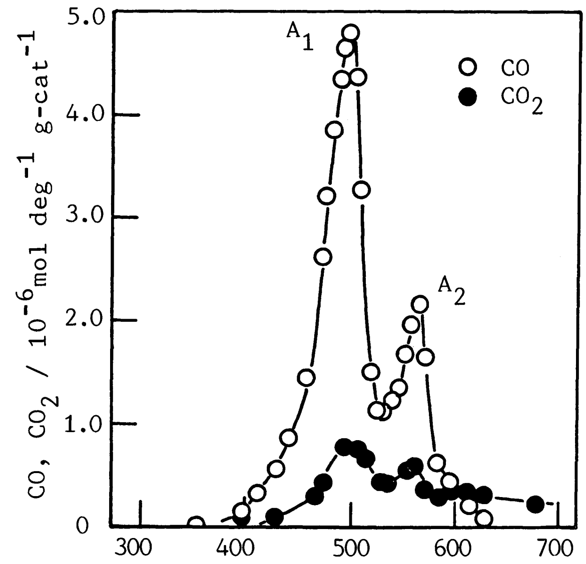

Fig.1. TPD spectra of CO and CO_2 on run 2 in Table 1. (The peaks A_1 and A_2 were observed at 473-500 K and 563-583 K, respectively, in other TPD runs.)

As shown in Table 1, the Rh-Y zeolite with lower rhodium content showed the higher ratio in A_2/A_1 under the same adsorption conditions. The values for the ratio of ($CO+CO_2$) against the number of rhodium atoms were found in the range of 2.0 - 2.4, suggesting that about two molecules of CO are adsorbed on each rhodium atom in both types of rhodium species for A_1 and A_2. The reduction of Rh(III) into $Rh(I)(CO)_2$ by the reaction with CO is accompanied with the formation of CO_2.[1] During the exposure of the Rh-Y zeolite to CO at 353 K, consumption of CO completed within 3 h. And the formation of CO_2 also completed within 3 h. Therefore, both of the rhodium species for A_1 and A_2 are thought to be $Rh(I)(CO)_2(L)$ species, while the ligand, L, in A_1 is different from that in A_2.

Table 1. Effects of adsorption conditions on the TPD of CO from the Rh-Y zeolite

Run	Rhodium	Adsorption conditions			Desorbed amounts/10^{-6}mol g^{-1}						($CO+CO_2$)/Rh
No.	content	CO	Temp	Duration	CO				CO_2	$CO+CO_2$	
	wt%	%	K	h	A_1	A_2	total	A_2/A_1			
1	2.0	30	353	5	242	37	279	0.15	150	429	2.2
2	2.0	30	393	5	268	70	338	0.26	106	444	2.3
3	2.0	30	433	5	44	277	321	6.30	112	433	2.2
4	2.0	30	393	10	230	119	349	0.52	120	469	2.4
5	2.0	10	393	5	109	157	266	1.44	126	392	2.0
6	0.7	30	393	5	11	83	94	7.55	66	160	2.4
7	1.0	30	393	5	54	81	135	1.50	92	227	2.3

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