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H_2-D_2 AND $^{16}O_2$-$^{18}O_2$ EXCHANGE REACTION ON Rh-Sn-γ-Al_2O_3 AND Ru-Sn-γ-Al_2O_3 IN RELATION TO THE SIMULTANEOUS REMOVAL OF NO AND CO

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The activation energy of the exchange reaction increases only slightly in H_2-D_2 and decreases significantly in $^{16}O_2$-$^{18}O_2$ by alloying Sn with Rh or Ru on γ-Al_2O_3. Tin promotes the activation of oxygen on Rh- or Ru-γ-Al_2O_3. The promoting effect of Sn in the removal of NO and CO in the presence of O_2 reported before[1,2] may be due to the activation of oxygen in the reaction.

The activity of γ-Al_2O_3 supported Rh and Ru for the removal of NO and CO in oxidative atmosphere is promoted by alloying with Sn.[1,2] In reductive atmosphere, the activity of Rh for the removal of NO and CO is not appreciably influenced[1] but that of Ru is lowered a little,[2] both by alloying with Sn. The effect of Sn on γ-Al_2O_3 supported Rh and Ru is studied by comparing the activities for such reactions as H_2-D_2 and $^{16}O_2$-$^{18}O_2$ (O_2-*O_2 in the following) isotope mixing.

The catalysts used were the same as those reported before,[1,2] i.e., both Rh and Ru were 0.5 wt % on γ-Al_2O_3 (E. Mercke), and Rh/Sn and Ru/Sn atomic ratios were unity. Weight percent of Sn in Sn-γ-Al_2O_3 was the same as those of the Sn-containing catalysts. The reactor was conventional closed system made of pyrex glass. The volume of the reactor was ca. 3 ml and contained 100 mg of one of the catalysts. The reactant gas was an equimolar mixture of H_2 and D_2, or that of $^{16}O_2$ and $^{18}O_2$. The catalysts were treated as described before.[1,2] After the reduction of the catalysts with H_2, the reactor was filled with He gas and allowed to stand for ca. 2 h in the low temperature bath. The catalysts were evacuated to 7×10^{-4}Pa just before introduction of the reactant gas. The reaction conditions are shown below; 77 to 478 K, $(7.2 \text{ to } 29) \times 10^3$Pa, 1 to 20 min. for H_2-D_2 exchange reaction, and 113 to 194.5 K, $(0.45 \text{ to } 7.4) \times 10^3$Pa, 1 to 20 min. for O_2-*O_2 exchange reaction. The reaction gas was analyzed by using a Hitachi RMU-6E mass spectrometer. D_2 (99.5 vol. %) was obtained from the Showa Denko K. K., Tokyo, and $^{18}O_2$ (99 atomic %) was obtained from the British Oxygen Co. Ltd., England.

The observed reaction order with respect to total pressure will be found by subtracting the exponent on Pa shown in Table from unity. Figures 1 and 2 show the Arrhenius-plot for H_2-D_2 and O_2-*O_2 exchange reactions, respectively, and the activation energy and pre-exponential factor calculated from figures 1 and 2 are

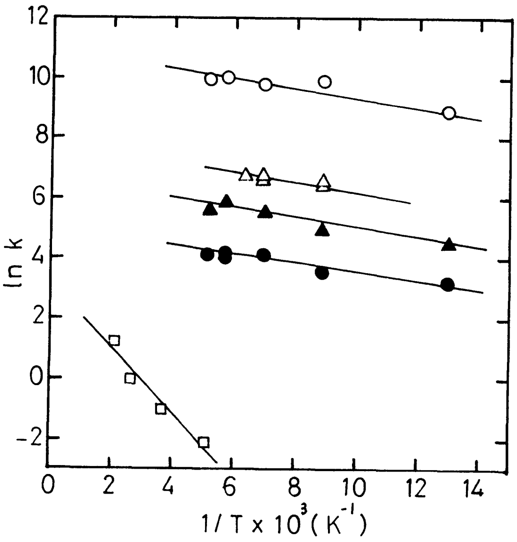

Figure 1 (left) Arrhenius-plot for H_2-D_2 exchange reaction

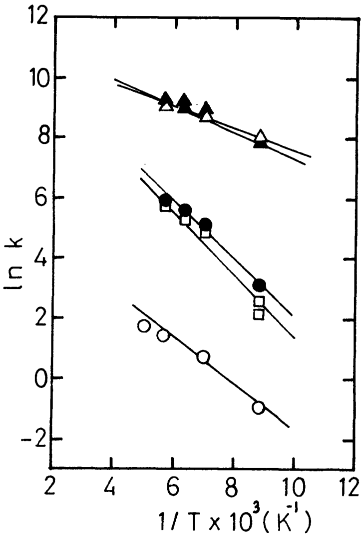

Figure 2 (right) Arrhenius-plot for O_2-$^*O_2$ exchange reaction

summarized in Table.

In the case of H_2-D_2 exchange reaction, activation energy increases slightly by alloying with Sn. The difference of the catalyst composition shows slight effect on H_2-D_2 exchange reaction, but shows significant effect on the removal of NO and CO on Ru.[2] Therefore, the activation of hydrogen in the reaction of NO and CO removal appears not to control the reaction.

The O_2-$^*O_2$ exchange reaction proceeds on Rh, Ru, and Sn in the same temperature range, and the activation energies are almost the same among these three. The alloying effect, however, is clearly observed by the decrease of activation energy. The promoting effect of Sn on this reaction is noteworthy in comparison with the slight effect of Sn on H_2-D_2 exchange reaction. The activation of oxygen in the reaction of NO and CO in the presence of O_2 seems to control the reaction over Rh-Sn-γ-Al_2O_3 and Ru-Sn-γ-Al_2O_3.

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Table Activation Energy (E) and Pre-exponential Factor (A)

	$H_2 + D_2$ = 2HD		$^{16}O_2 + ^{18}O_2 = 2^{16}O^{18}O$	
Catalysts	E(KJ/mol)	A[a]	E(KJ/mol)	A[a]
Rh	1.0	$3.6 \times 10^4 Pa/Z$	7.6	$7.3 \times 10^2/Z$
Rh/Sn = 1	1.1	$2.0 \times 10^3 Pa^{0.5}/Z$	3.2	$8.8 \times 10^4 Pa/Z$
Ru	1.0	$1.3 \times 10^2 Pa^{0.2}/Z$	7.8	$1.0 \times 10^5 Pa^{0.5}/Z$
Ru/Sn = 1	1.4	$7.8 \times 10^2 Pa^{0.4}/Z$	3.8	$1.5 \times 10^5 Pa/Z$
Sn	8.8	$1.6 \times 10/Z$	8.5	$1.1 \times 10^5 Pa^{0.5}/Z$

a: Z = (min.) x (g-catalyst)

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