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ON THE ACTIVE SPECIES IN THE REDUCED OR PARTIALLY REOXIDIZED RHENIUM OXIDE-ALUMINA CATALYST FOR THE METATHESIS OF PROPENE

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Novel methods for the activation of Re_2O_7-Al_2O_3 metathesis catalyst, the reduction of the catalyst with propene and the adsorption of oxygen on the reduced catalyst, provide highly active catalysts for the metathesis of propene at low temperatures near 50°C. The properties of the active sites were estimated by their kinetic behavier, EPR studies, etc.

Re_2O_7-Al_2O_3 is one of the most effective catalysts for the metathesis of alkenes, since it is highly active even at room temperature,[1-3] and effective not only for inner alkenes but also for branched alkenes[4] and 1-alkenes.[1] However, the activity of the catalyst remarkably varies with its Re contents, and usually the activity of the catalyst containing small amounts of Re (<1 atom%) is abnormally low. This suggests that only a small part of Re in the catalyst plays a role in the catalytic activity when the catalyst is activated by a conventional method. It is important to study on the effect of the pretreatment of the catalyst and the nature of the active sites in the improvement of catalytic activity. In particular, high prices of rhenium compounds and the volatility of Re_2O_7 demand the investigation of the catalyst with lower Re contents to reveal the latent active sites on the catalyst.

We had already reported that the activity of the Re_2O_7-Al_2O_3 catalyst was stimulated by the addition of various metal oxides such as WO_3, V_2O_5, etc. and the activities of the modified catalysts (Re_2O_7-Me_xO_y-Al_2O_3; Re/Al=1/199, 1/99, Me/Al=5/95, 10/90) were well correlated with the electronegativities of the added metal ions, where the adsorption of alkenes was promoted by the induced effect of them.[1]

Now, this letter deals with the preparation and the properties of two kinds of active sites for the metathesis of propene, one of which is formed during the reaction at relatively low temperatures (~ 50°C) on the 0.5 atom% Re_2O_7-Al_2O_3 catalyst pretreated with propene at 500°C and the other is produced by the adsorption of oxygen on the propene-pretreated catalyst.

The Re_2O_7-Al_2O_3 (0.5 atom% of Re) catalyst was prepared by impregnating γ-alumina with an aqueous solution of rhenium heptoxide. The details on the preparation of the catalyst were described in the preceeding paper.[3] The catalysts were activated in situ before the reaction by means of three methods as follow.

Method-He———Helium-treatment (a conventional treatment): The catalyst was activated in the atmosphere of flowing dry oxygen-free helium for 3 hr at 500°C and then cooled to a reaction temperature.

Method-Pr———Propene-treatment: The catalyst was dried by flowing helium at 500°C for 0.5 hr and treated by flowing propene at 500°C for 2 min, followed by purging propene with helium again for 2 hr at the same temperature and then cooled in flowing helium to the reaction temperature.

Method-Ox———Oxygen-adsorption: The catalyst was activated by Method-Pr, followed by contacting with dry oxygen at a reaction temperature of 50°C by means of a pulse method and then used for the reaction. The amount of oxygen adsorbed was determined by the use of a conventional thermal conductivity cell.

The reaction was conducted in a conventional fixed bed flow reactor in the range of about 20°C to 90°C, mainly at 50°C, under an atmospheric pressure of propene, of which flow rate was set at 0.756 l/hr. Four grams of the catalyst (0.5 atom% Re) were used for each run (W/F=1.32 g·hr/l). The EPR spectra of the catalysts were taken with a JEOL-PE-2X spectrometer operating at 9.4 GHz.

Activity of Helium-treated catalyst

Dashed lines in Fig.1 show the activity changes of the 0.5 atom% Re_2O_7-Al_2O_3 catalyst activated by Method-He for the metathesis of propene at reaction temperatures of 50, 70, and 90°C. The initial activity and the rate of deactivation of the catalyst increased with the raise of the reaction temperature, which is a typical behavior of the active site produced by a conventional pretreatment. The rate of deactivation was represented by a typical first-order reaction for the number of the active site. The activation energy for the rate of the deactivation was 5.1 kcal/mol-site and that for the rate of the metathesis at t=0 was 6.6 kcal/mol.

Activity of Propene-treated catalyst

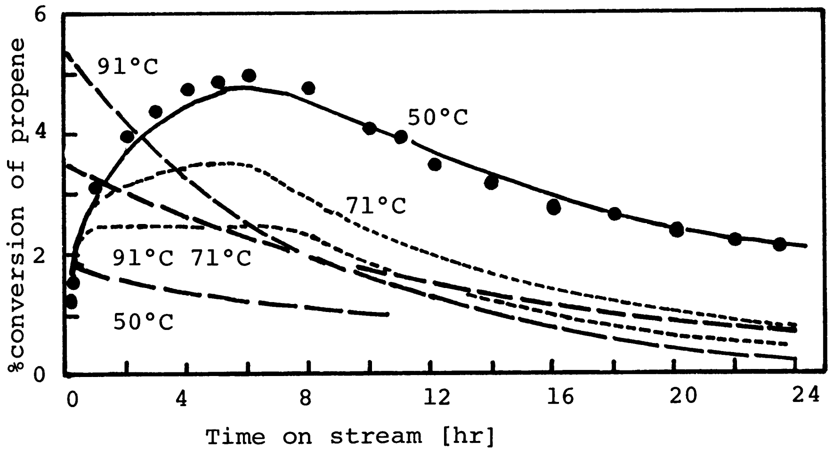

Fig.1 The activity change of the helium-treated or the propene-treated Re_2O_7-Al_2O_3 catalyst with the time on stream of propene at 50,71,and 91°C.
——:He-treatment, ------, ●; C_3H_6-treatment,
•—:The line obtained from equation (1).

Dotted curves and circles in Fig.1 show the time course of the activity of the Re_2O_7-Al_2O_3 (0.5 atom% of Re) activated by Method-Pr for the metathesis of propene at 50, 70, and 90°C. The profile of the activity change at 50°C suggests that there are two kinds of active sites on the catalyst; one is a relatively stable but less contributive site and the other is the active site which varies with the time on stream of propene. The former, Site 1, is the same site as formed by Method-He but the amount of it is minor. The latter, Site 2, appeares during the reaction, of which number increases up to a maximum value near t=6 hr and then decreases gradually with the time on stream of propene. The appearance-disappearance process for Site 2 is irreversible under our conditions, since the process does not proceed in the absence of propene. The solid curve in Fig.1 shows the theoretical line calculated by equation (1) based on an irreversible first-order consecutive reaction model for the transmutation of Site 2.

$$x = x_2 + x_1 = 11.9 \left\{\exp(-0.110t) - \exp(-0.239t)\right\} + 1.5 \qquad (1)$$

where x_2, x_1 or x is the % conversion of propene to ethene and 2-butene at t=t hr over Site 2, Site 1, or Site 1 + Site 2, respectively.

The deformation of the profile of the conversion at 70°C or 90°C in Fig.1 is believed to be due to the increase in the contribution of Site 1 to the total conversion, in particular at the initial stage of the reaction. However, it is still strange that the activity due to Site 2 decreases with the increase in the reaction temperature as can be seen in Fig.1 again. In order to clearify whether the unusual behavior or the change of the number of the active site, the temperature jump study was tested. When the reaction temperature was lowered rapidly from 89°C to 50°C during the reaction, the catalytic activity once fell and then began to increase gradually in the same manner as the profile of the activity change at 50°C. This result shows that the decrease in the activity with the increase in the reaction temperature in Fig.1 is due to the decrease in the number of the active site or the rate of its formation, while the activity per the number of active site increases with the reaction temperature, which is a usual behavior. The mechanism of the creation of Site 2 is not clear in this stage. However the results suggest that a coordination of a certain species to deeply reduced Re ions, viz the precursor of Site 2, is an important process in the formation of Site 2. We can expect from this consideration that the adsorption of an appropriate compound on the pre-reduced Re_2O_7-Al_2O_3 catalyst produces a highly active catalyst. First of all, we tested the effect of oxygen adsorption.

Effect of oxygen adsorption on the reduced catalyst

A highly active catalyst was obtained by the adsorption of oxygen on the propene-treated catalyst at the reaction temperature before and during the reaction, as can be seen in Fig.2. The initial activity was found to be proportional to the amount of oxygen adsorbed. The oxygen-adsorbed catalyst has three kinds of EPR signals; a sharp line with g=2.00, a six-line signal with $g \fallingdotseq 2.25$ and $A \fallingdotseq 780$ gauss which also appeare on the reduced catalyst,1-3) and an aisotropical signal with $g_{\parallel} = 2.038$ and $g_{\perp} = 2.003$ which is formed by the adsorption of oxygen on the reduced catalyst as can be seen Fig.3 (b). The shape of the EPR signal in Fig.3 (b) indicates that the unpaired electron presents in the field with axial symmetry. This signal did not appeare on Al_2O_3. The intensity of this signal decreased with the time on stream in the same manner as the catalytic activity. The same phenomena were observed for the catalyst pre-reduced with hydrogen instead of propene. Shelef5) who also observed a similar EPR signal on the air-exposed Re^0-Al_2O_3 sample suggested that the signal was based on the Re^{2+} ion with O_2^{2-} as a ligand. However, we may assign this signal to O_2^- on low valent Re ions or Al ions adjacent to them, since the profile and g-values of the signal agrees with O_2^- on Al_2O_3 reported by Losee6) who employed N_2O as an oxidant instead of O_2. In either case, it was considered that the active site for the metathesis reaction under our conditions is a relatively

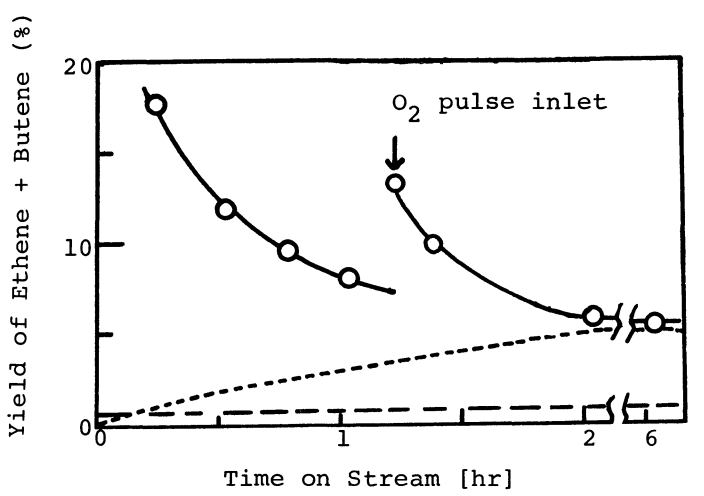

Fig.2 Effect of oxygen adsorption on the propene-treated Re_2O_7-Al_2O_3 on its catalytic activity.

—o— :Method-Ox, ---- :Method-Pr, — — :Method-He

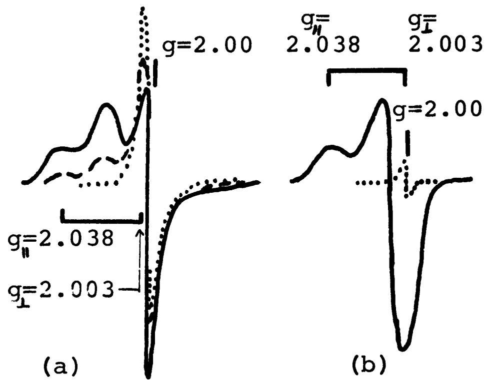

Fig.3 EPR spectra of reduced catalysts before(dotted lines) and after(solid lines) the adsorption of oxygen

a) Reduced with propene(Method Pr)
b) with hydrogen at 500°C for 10 min.
— — — :after contacting propene for 1 hr

low valent Re ion, for instance $Re^{+} \sim Re^{4+}$ with O_2^{-} or O_2^{2-} as a ligand.

The difficulties in controlling the oxidation state of Re by the reduction of the catalyst with propene, hydrogen or other reducing agents and the requirment of high-temperature treatment of the catalyst in order to remove water from the catalyst limit the yield of such an appropriate valence state of Re ion. Our method, reducing Re_2O_7 to a low valent Re and removing water from the catalyst at the elevated temperature, followed by selectively reoxidizing it at mild conditions, provides a highly active catalyst for the metathesis reaction. The amount of oxygen adsorbed on the catalyst suggests that more than 20% of Re in the catalyst is working (turnover number=1x0.1 sec^{-1}). Now, we are studying on the thermal stability of this ligand and the effect of other ligands. Details on these will be reported elswhere in the near feature.

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