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SURFACE STRUCTURES OF FIXED Cr CATALYSTS AND THEIR CATALYTIC ACTIVITIES FOR CO OXIDATION AND C_3H_6 HYDROGENATION

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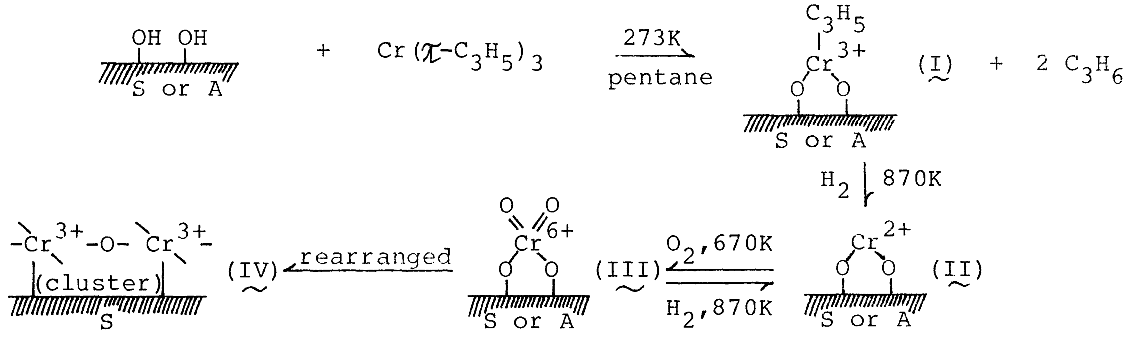
Two types of active fixed Cr catalysts(Al_2O_3 and SiO_2 supports) and surface structures of active sites are reported. Coordinatively unsaturated Cr^{2+} ions with three vacant positions in the "virgin" fixed catalyst showed a high activity for C_3H_6 hydrogenation. Five-coordinated Cr^{3+} species with suitably strong exchange interaction between Cr^{3+} in a Cr^{3+}-O-Cr^{3+} cluster of the "rearranged" fixed catalyst created by surface reconstruction were found to be active sites for CO oxidation.

Elucidating the origin of catalytic activity and selectivity of a supported catalyst has been one of major challenges in catalytic chemistry.1) However, the essential factors for catalysis are generally indefinite because of heterogeneous and ill-defined properties of catalyst surfaces. Preparations of active catalysts have also been another important subject from physico-chemical points of view as well as industrial interests.2) In the present study we wish to report catalytic activities of two types of fixed Cr catalysts, and the structures and the chemical nature of active sites for CO oxidation and C_3H_6 hydrogenation.

The fixed Cr catalysts were prepared according to the following scheme,



taking advantage of the facile reaction[3] between $Cr(\pi\text{-}C_3H_5)_3$ and surface OH groups of silica(S) or alumina(A), followed by H_2 and O_2 treatments. The Cr content, Cr/SiO_2 or Cr/Al_2O_3, in all catalysts employed was 0.9 wt%.

(1) CO Oxidation with O_2 over SiO_2-Support Cr Catalysts

The CO oxidation was studied in a closed circulating system in the temperature range 373-550K. The structure, $>Cr\begin{smallmatrix}\neq O\\ \neq O\end{smallmatrix}$, of the fixed catalyst(III) showed a low activity. The activity of a usual impregnation Cr catalyst with monochromate (380nm) and dichromate(460nm) structures involving small amounts of Cr^{3+} species was also low. However, the "rearranged" fixed catalyst(IV) which was prepared by the redox treatment of the catalyst(III) at 848K, was found in fig.1 to have a higher activity by a factor of more than 30, than the impregnation catalyst as well as the catalyst(III). The activation energies were obtained to be 12.5 KJ/mol (catalyst(IV)), 89.9 KJ/mol(impreg.cat.) and 40.3 KJ/mol(Cr_2O_3).

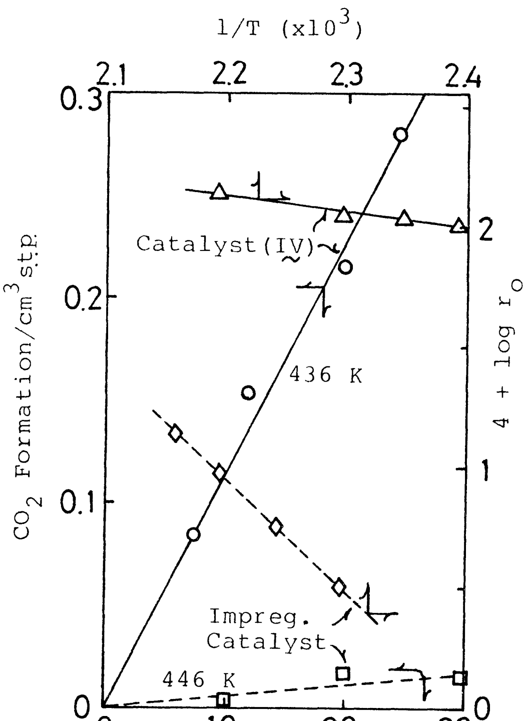


Fig.1 CO oxidation with O_2 over the rearranged fixed catalyst(IV) and the impregnation catalyst;
catalyst=0.2 g,
catalyst(IV):CO=16.3 Torr
O_2=16.3 Torr
impreg.cat. :CO=24.0 Torr
O_2=40.0 Torr

The surface environments of the catalyst(IV) and the impregnation catalyst were considerably different; the latter catalyst luminesced at 16.4-17.2 kK by the excitation of the Cr-O charge transfer band of isolated monochromate species, while the catalyst(IV) showed no significant emission. Again the photoluminescence technique illustrated the surface heterogeneity of the impregnation catalyst. In a UV diffuse reflectance spectrum of the catalyst(IV) chromate structures reduced relatively and large amounts of square pyramidal(or trigonal bipyramids) Cr^{3+}(350, 590,>900nm) and octahedral Cr^{3+}(270, 440, 630nm) structures developed. The Racah parameter(B_{35}) in ligand field theory which correlates with the strength of the Cr^{3+}-Cr^{3+} interaction[4] was calculated to be 705 cm^{-1}(Δ=15870cm^{-1}, δE=6850cm^{-1}) for the catalyst(IV) and 885 cm^{-1}(Δ=15620cm^{-1}, δE=7900cm^{-1}) for the impregnation catalyst. The B_{35} of Cr_2O_3 was in the range 480-760 cm^{-1}, depending upon the nature of Cr_2O_3 gels. The large amounts of β-phase Cr^{3+}clusters(Cr^{3+}/total Cr=35%, g=1.976) in the catalyst(IV) were also observed by an ESR spectroscopy. The impregnation catalyst involved Cr^{3+} of 6%. The peak widths(ΔH) of the ESR spectra were found to be 850 G(catalyst(IV)) and 1080 G(impreg.cat.), while that of α-Cr_2O_3 is 440-500 G.[5)] The signal was not observed at 77K due to antiferromagnetism. The ΔH may be explained as a measure of the strength of exchange interaction between Cr^{3+} ions. Thus it is obvious from the values of B_{35} and ΔH that the Cr^{3+}-Cr^{3+} interaction in the rearranged fixed catalyst is stronger than that in the impregnation catalyst, but weaker than the strong interaction of a crystalline Cr_2O_3. The volumetric data(O_2 & CO adsorptions at 201-413K over catalysts evacuated at 843K) indicated that there is one coordination position per a Cr^{3+} ion involving a minor portion of two vacant sites.

The active structure of CO oxidation with O_2 is, consequently, concluded to be the five-coordinated Cr^{3+} species having suitably strong exchange interaction (a little longer than 2.65 Å) between Cr^{3+} ions in a Cr^{3+}-O-Cr^{3+} cluster structure. This structure could be prepared from Cr^{6+} species fixed on originally acidic OH groups of silica, but not obtained from chromate structures located on anionic OH groups.

(2) C_3H_6 Hydrogenation over Al_2O_3-Support Cr Catalysts

The deuterium addition to C_3H_6 over fixed and impregnated Cr catalysts proceeded in the temperature range 195-263K. The surface complex(I) was converted to the "virgin" catalyst(II) with H_2 at 870K, releasing the allyl ligand; the allyl ligand was decomposed to C_1, C_2, C_3 and C_4 hydrocarbons. The stoichiometric uptakes of O_2 and H_2 in the oxidation and reduction in the synthesis scheme clearly revealed that the oxidation state of Cr ions of the catalyst(II) is divalent. According to N_2 and O_2 adsorptions in the range 175-191K, the grey virgin catalyst had two and/or three vacant coordination sites per unit Cr, while the corresponding impregnation catalyst(light blue) with $Cr^{2.15+}$ showed only one vacant site. The fixed catalyst with coordinatively unsaturated Cr^{2+} ions was much more active than the reduced impregnation catalyst as shown in fig.2. The activation energy of the reaction on the catalyst(II)(14.6 KJ/mol) was lower than those for the impregnation catalyst(22.7 KJ/mol) and for Cr_2O_3(15.1 KJ/mol). An impregnation catalyst showed the maximum activity at the Cr oxidation state just below trivalency(3.5 times higher than $Cr^{2.15+}$ catalyst). It has been demonstrated[6)] that Cr^{3+}(cus)-O^{2-}(cus) pairs at a chromia surface functioned as active sites. Isolated trivalent Cr(catalyst(I)) without active oxygen ligands was almost inactive even if they are coordinatively unsaturated. Therefore Cr^{3+} ions obviously require oxygen dianion

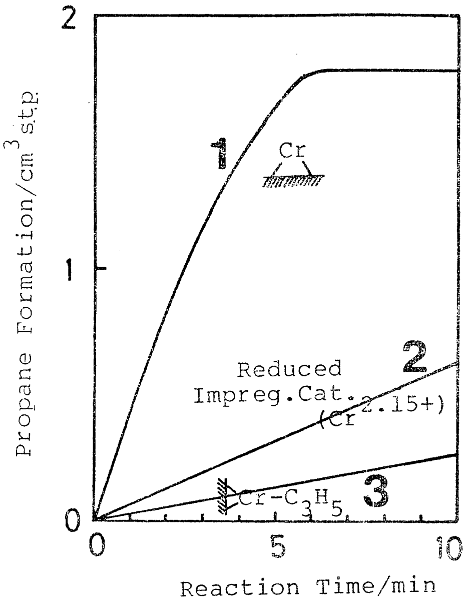
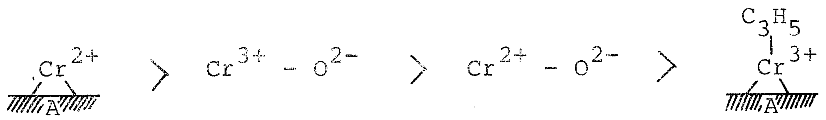


Fig.2 Deuterogenation activities of fixed and impregnation catalysts at 238K; C_3H_6=8.1 Torr, D_2=46 Torr

for activity. However, the most active structure for C_3H_6 hydrogenation was found to be the coordinatively unsaturated divalent Cr ion with probably three vacant sites. The amount of propane formed in the reaction, $C_3H_{6(ad)}$ (at saturation)$+H_2 \rightarrow C_3H_8$, suggested that C_3H_6 occupied one coordination site on a Cr^{2+} during hydrogenation. H_2(weakly adsorbed) may be "oxidatively" dissociated on vacant coordination positions of Cr^{2+}, while on usual oxide catalysts with Cr-O pair sites[7] it is "heterolytically" dissociated.

The active Cr^{2+} species of the virgin catalyst obeyed unfavorable, "environmental" change by oxidation and reduction treatments to lead a considerable decrease in activity. This may be the reason why the active Cr^{2+} structure could not be created by a usual impregnation method which requires a redox treatment for catalyst activation. The catalytic activity of the virgin catalyst(II) was completely restored by H_2 treating for 2 hours at 295K when neccessary.

The order of activity for surface structures is shown as follows;



$$Cr^{2+} > Cr^{3+} - O^{2-} > Cr^{2+} - O^{2-} > \overset{C_3H_5}{Cr^{3+}}$$

References

1) Y.Iwasawa, Y.Nakano and S.Ogasawara, J.C.S.Faraday I, 74,2968(1978); Y.Iwasawa et at., ibid., 75,1465(1979)

2) Proc.2nd Internat.Symp.Prep.Catal.,Belgium(1978), ed. B.Delmon, P.Grange, P. Jacob and G.Poncelet(1979)

3) G.H.Ballard, Advan.Catal., 23,263(1973); Yu.I.Yermakov et al., ibid., 24,137 (1975); J.P.Candlin et al., Advan.Chem.Ser., 132,212(1974)

4) D.Reinen, Struct.Bonding(Berlin), 6,30(1969)

5) Yu.I.Pecherskaya et al., Kinet.Catal., 3,90(1962); V.B.Kazanskii et al., 1,232 (1960)

6) R.L.Burwell Jr., G.L.Haller, K.C.Taylor and J.F.Read, Advan.Catal., 20,1(1969)

7) R.L.Burwell Jr. and K.S.Stec, J.Colloid Interface Sci., 58,54(1977)

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