Synergistic Catalysis by Catalysts derived from $Fe_{3-x}Ru_x(CO)_{12}$ (x = 0,1,2,3) supported on γ-Al_2O_3

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The catalysts derived from $Fe_{3-x}Ru_x(CO)_{12}$ (x = 0,1,2,3) supported on γ-Al_2O_3 functioned as active catalysts for CO hydrogenation, C_2H_4 self-homologation, and C_2H_6 hydrogenolysis, synergistic effects being observed particularly in the last two reactions.

Inorganic oxide-supported mixed metal clusters may provide a new method of preparation of synergistically-promoted catalysts as well as new chemistry. There have only been a few reports of supported mixed metal cluster catalysts.[1] This communication reports the properties of catalysts derived from $Fe_{3-x}Ru_x(CO)_{12}$ (x = 0,1,2,3)/γ-Al_2O_3 in carbon monoxide hydrogenation, ethene self-homologation, and ethane hydrogenolysis.

Impregnation of $Fe_2Ru(CO)_{12}$,[2] $FeRu_2(CO)_{12}$,[2] and $Ru_3(CO)_{12}$ onto γ-Al_2O_3 was carried out by addition of γ-Al_2O_3 (150 $m^2 g^{-1}$, pretreated at 573 K for 2 h) to pentane solutions of these clusters in an Ar flow (99.9995% purity), followed by evacuation of solvent at room temperature. $Fe_3(CO)_{12}/Al_2O_3$ was obtained using a dry mixing method under vacuum.[3] The catalytic reactions were conducted in a closed circulating system.

Previous work[3] demonstrated that $Fe_3(CO)_{12}$ was stabilized on the γ-Al_2O_3 surface (OAl<), by the formation of a surface species $[HFe_3(CO)_{10}(OAl<)]$, with a resultant large shrinkage of the Fe_3 framework. Interactions of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, and $Ru_3(CO)_{12}$ with γ-Al_2O_3 also suggested the formation of the surface species, $[HFe_2Ru(CO)_{10}(OAl<)]$, $[HFeRu_2(CO)_{10}(OAl<)]$, and $[HRu_3(CO)_{10}(OAl<)]$, respectively.[4] The temperature desorption spectra (TDS) of supported Fe_3 or Ru_3 carbonyl clusters exhibited negligible or very small CH_4 peaks compared with large CO, H_2, and CO_2 peaks, whereas on the supported mixed metal clusters a large CH_4 peak at *ca.* 610 K was observed. The TDS of a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters supported on the Al_2O_3 was the same as a superposition of the spectra of the individual supported clusters.

The supported clusters were heated to 493 K under vacuum and then reduced with H_2 at 723 K for 1 h. The products of CO hydrogenation on the catalyst thus obtained from $Fe_3(CO)_{12}$ were CO_2 (71%) and hydrocarbons (29%; mainly CH_4) under conditions of CO = H_2 = 150 Torr and 473 K. The replacement of an Fe atom of the cluster by a Ru atom increased the activity by a factor of *ca.* 50, as well as the selectivity towards C_2—C_5 hydrocarbons by a factor of 6.2 (74.2%; alkene fraction 94%). On further replacement of Fe atoms by Ru atoms the good selectivity was retained. In contrast, conventional Fe–Ru catalysts, prepared by impregnation using an aqueous solution of $Fe(NO_3)_3$ and $RuCl_3$, produced predominantly CH_4 under identical conditions.

The activities of the Fe–Ru impregnation catalysts for C_2H_4 self-homologation at 523 K reduced with a decrease in the Ru content as shown in Figure 1. The ratio of propene/butene product was almost independent of the Ru/Fe ratios and the Fe impregnation catalyst was almost inactive. These results suggest that active Ru sites did not interact with the Fe component. However, the mixed metal cluster-derived catalysts were more active than the catalysts obtained from $Ru_3(CO)_{12}$ or $Fe_3(CO)_{12}$. The $FeRu_2$ cluster-derived catalyst showed the maximum activity among the catalysts derived

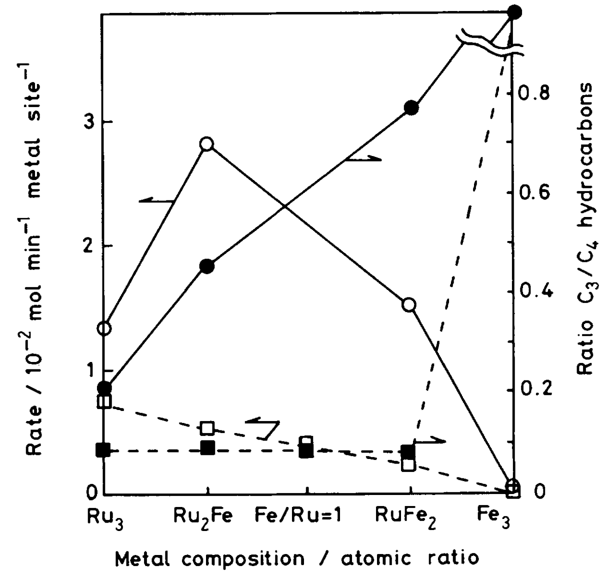

Figure 1. C_2H_4 Self-homologation on Al_2O_3-supported $Ru_3(CO)_{12}$, $FeRu_2(CO)_{12}$, $Fe_2Ru(CO)_{12}$, and $Fe_3(CO)_{12}$ catalysts (○,●), and impregnation Fe/Ru catalysts (□,■) at 523 K; C_2H_4 = 33 Torr; metal = 6.0 × 10^{-5} mol; metal/support = 1.5—3 wt%. Butene production was negligible on both types of Fe catalysts.

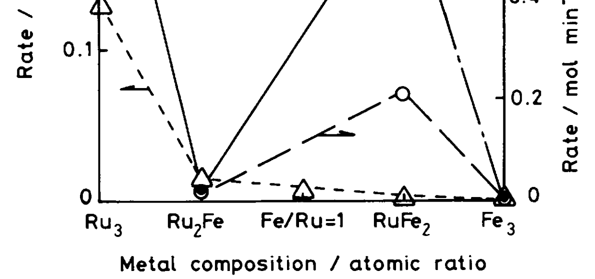

Figure 2. Ethane hydrogenolysis over Al_2O_3-supported $Ru_3(CO)_{12}$, $FeRu_2(CO)_{12}$, $Fe_2Ru(CO)_{12}$, and $Fe_3(CO)_{12}$ catalysts (●,○), and impregnated Fe/Ru catalysts (△). Reaction temp. = 443 K; ethane = 25 Torr; H_2 = 50 Torr.

from the $Fe_{3-x}Ru_x(CO)_{12}$ (x = 0,1,2,3) clusters, Figure 1. The Fe_2Ru catalyst was also more active than the Ru_3 catalyst. The active sites of the mixed metal cluster catalysts consist of Fe^{II} ions and small Ru clusters chemically bonded to the Al_2O_3 surface through the surface oxygen atoms, as determined by the extended *X*-ray absorption fine structure studies.[4] The steadily increasing selectivity (C_3/C_4 ratio) with increasing Fe content, Figure 1, for the supported cluster catalysts in contrast to the impregnation catalysts reflects the effect of Fe^{II} ions when adjacent to the Ru clusters.

Ethane hydrogenolysis proceeded more readily on the Ru_3 cluster-derived catalyst than on the impregnation Ru catalyst, as shown in Figure 2. The Fe catalysts were inactive. The activities of the impregnation catalysts decreased with a decrease in the Ru content of the catalyst. The Fe_2Ru cluster catalyst showed more than one order of magnitude greater activity than the $FeRu_2$ catalyst. Ethane hydrogenolysis obviously requires a different structure and arrangement of active sites from those for C_2H_4 self-homologation. The Ru-co-ordination number around a Ru atom was twice as large in the $FeRu_2$ catalyst than in the Fe_2Ru catalyst.

The origin of the synergistic effects observed with the $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$-derived catalysts is unclear at present, but the action of these catalysts is significantly different from that observed on the conventional impregnation catalysts.

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References

1 J. R. Anderson and D. E. Mainwaring, *J. Catal.*, 1974, **35**, 162; M. Ichikawa, *ibid.*, 1979, **56**, 127; 1979, **59**, 67; R. Pierantozzi, K. J. McQuade, B. C. Gates, M. Wolf, H. Knözinger, and W. Ruhmann, *J. Am. Chem. Soc.*, 1979, **101**, 5436; J. R. Budge, J. P. Scott, and B. C. Gates, *J. Chem. Soc., Chem. Commun.*, 1983, 342; J. R. Budge and B. C. Gates, *Pan-Pac. Synfuels Conf.*, 1982, **1**, 204; A. Choplin, M. Leconte, J. M. Basset, S. G. Shore, and W. L. Hsu, *J. Mol. Catal.*, 1983, **21**, 389; L. Bruce, G. Hope, and T. W. Turney, *React. Kinet. Catal. Lett.*, 1982, **20**, 175.

2 D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A*, 1969, 502.

3 Y. Iwasawa, Y. Yamada, S. Ogasawara, Y. Sato, and H. Kuroda, *Chem. Lett.*, 1983, 621.

4 K. Asakura, M. Yamada, Y. Iwasawa, and H. Kuroda, unpublished results.