

NOTE

Use of a Bimetallic Molecular Cluster Compound for the Preparation of a Dispersed Bimetallic Catalyst: Methylcyclopentane Hydrogenolysis

Recent studies on supported metal catalysts have focused increasing attention upon bimetallic systems. The electronic structure of the dispersed metal and hence its catalytic activity is largely dependent upon phase composition. This has been recognized in recent publications where the degree of alloy formation has been investigated by both reaction activity and chemisorption. These techniques have been applied to bimetallic metal systems where the bulk phase composition indicates various degrees of miscibility.

The extent to which alloy particles are formed nevertheless remains a matter of some uncertainty. For instance, Sinfelt (1) has reported evidence based on catalytic and gas adsorption studies for the existence of bimetallic particles in Ru-Cu and Os-Cu systems, although these are metal pairs having almost total immiscibility in the bulk. On the other hand, Anderson, Conn and Brandenberger (2, 3), using particle size measurements by X-ray diffraction line broadening together with hydrogen chemisorption measurements, concluded that in Rh-Ag the particle composition agreed with the expectations from the bulk behavior where the miscibility is known to be low. The theory of solution stabilization by small particle size effects is also in some disarray, with Ollis (4) concentrating on surface energy effects, while Hoffmann (5) has criticized Ollis's work at a quantitative level, and has concentrated on possible kinetic stabilization by suppression of phase separation mechanisms.

Studies of supported dispersed bimetallic catalysts, including Sinfelt's "clusters," have been carried out either upon catalysts prepared by conventional impregnation methods, or by ion exchange methods.

In this note we draw attention to an alternative preparative approach and present preliminary results for the behavior of the resulting catalyst in methylcyclopentane hydrogenolysis. Our approach is based on the utilization of molecular bimetallic cluster compounds containing the two metals in known proportions with known stereochemical structure. These molecular cluster compounds contain heterometallic bonds, and they contain only very few—typically 4 or 6 metal atoms—arranged in either tetrahedral or octahedral structure. We propose that these molecular bimetallic cluster compounds may be used as specific precursors for the generation of dispersed bimetallic catalysts.

We illustrate this here by the use of the molecular cluster compound $[\text{Co}_2\text{Rh}_2](\text{CO})_{12}$ as the precursor. This was deposited (under a nitrogen atmosphere) from a hexane solution onto Degussa 200 silica support of surface area $200 \text{ m}^2 \text{ g}^{-1}$ so as to yield a total metal loading of 1 wt%. The hexane solvent was removed under vacuum in a rotary evaporator at room temperature. Removal of CO was accomplished by slowly heating the material to 300°C in a stream of dry nitrogen where it was maintained for 3 hr. Finally, it was reduced overnight in a pure hydrogen stream at 380°C . A sample of reduced catalyst was

TABLE 1
TYPICAL PRODUCT DISTRIBUTIONS AS A FUNCTION OF SPACE VELOCITY (wt %)

WHSV (g g ⁻¹ hr ⁻¹)	C ₁ -C ₄	C ₅ ^a	C ₆ ^b	Bz ^c	223TMB ^d	cH ^e
11.36	0.08	0.07	2.07	0.02	0.02	0.15
45.45	0.03	0.03	1.01	Tr ^f	0.01	0.10
113.64	0.01	0.02	0.55	Tr	0.01	0.09

^a C₅ isomers: isopentane, *n*-pentane, cyclopentane.

^b C₆ isomers: 2-methylpentane, 3-methylpentane, *n*-hexane.

^c Bz: benzene.

^d 223TMB: 2,2,3-trimethylbutane.

^e cH: cyclohexane.

^f Tr: trace.

outgassed at 380°C for 14 hr; the hydrogen adsorption measured at 25°C and 200 Torr gave a value of $H_s/M_t = 0.22$. This value was not altered by either reduction (5 hr) and outgassing (14 hr) at 500°C, or by an initial oxygen treatment at 315°C to remove possible carbon contamination from the decomposition of CO followed by a similar reduction and outgassing at 500°C. Clearly, some particle aggregation has occurred although no strong evidence for this was seen by high resolution electron microscopy. A full account of the preparative and characterization details will be reported shortly (6).

This catalyst was examined for reactions of methylocyclopentane (MCP) in the presence of excess hydrogen. Reactions were

carried out in a stainless steel microreactor system operating in the continuous flow mode. Analysis of the product stream was by capillary column gas chromatography. The starting material was Matheson Colman & Bell 99 + mol% MCP, the purity of which was checked by sampling the inlet stream. High purity hydrogen was used as the carrier gas.

The reaction conditions used in MCP hydrogenolysis were: molar H₂/MCP ratio 6.9, temperature 260°C, pressure 42.7 psia. The degree of conversion was kept low, less than 3%, to decrease possible secondary reactions. Typical product distributions at various space velocities are shown in Table 1. The product distribution illustrates a remarkable specificity for hydrogenolysis of

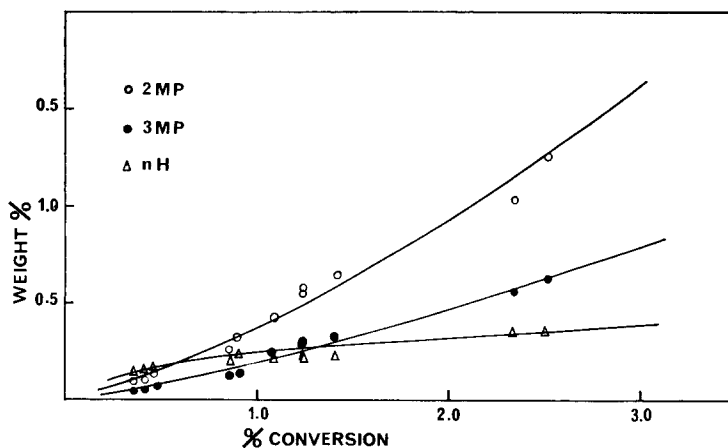


FIG. 1. Hexane isomer formation as a function of total methylocyclopentane conversion.

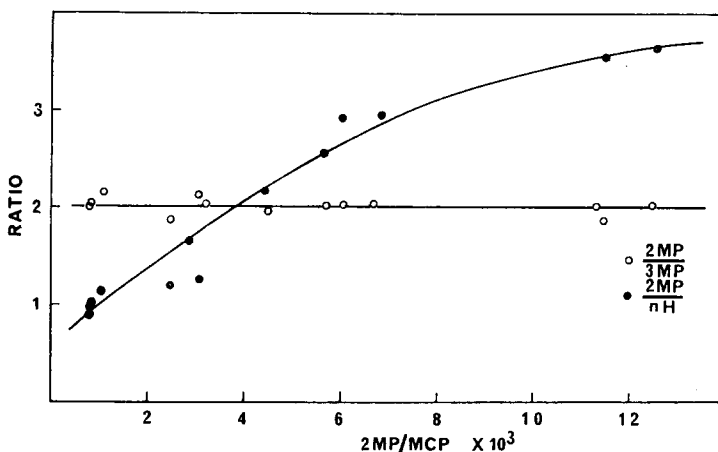


FIG. 2. Variation of hexane isomer ratio as a function of extent of 2-methylpentane formed.

the methyl-substituted 5-membered ring to noncyclic C_6 isomers with little ring expansion to cyclics and even less extensive cracking to lower molecular weight products. This can be compared to the hydrogenolysis activities of Group VIII noble metal powders as studied by Carter, Cusumano and Sinfelt (7). Here a reaction temperature of only 113°C for the hydrogenolysis of *n*-heptane was necessitated by the reactivity of rhodium powder, the activity of which was only exceeded by ruthenium within this group of metals. From the hydrogenolysis of ethane (8) and *n*-hexane (9) the activity (expressed as the specific reaction rate at about 200°C) of cobalt can be estimated to be only about one order of magnitude less than that of rhodium.

In Fig. 1 the product distribution is shown as a function of the total MCP conversion. This product distribution remained constant with increasing catalyst use. Judging from the existing data there is a considerable dissimilarity in the behavior of our Co-Rh catalyst and conventional rhodium and cobalt catalysts. Thus rhodium powder (8) and supported cobalt (9) catalysts give terminal carbon-carbon bond rupture with *n*-alkanes, although rhodium also gives rather more general fragmentation. Moreover, the reaction of methylcyclopentane on a rhodium film catalyst (10) gives a reaction that is heavily weighted towards general fragmentation

and the formation of methane. On the other hand, the present reaction of methylcyclopentane over the Co-Rh catalyst gives a ring opening reaction very reminiscent of the behavior of dispersed platinum (11-13) and the extent of general fragmentation is very small.

To examine the isomer ratios more closely, Fig. 2 shows the variation of the ratios 2-methylpentane/3-methylpentane and 2-methylpentane/*n*-hexane as a function of the extent of 2-methylpentane formed, the latter being used as an index of the extent of conversion. From these plots the constant ratio for 2-methylpentane/3-methylpentane of 2 with increasing conversion indicates that the initial statistical ring opening in these positions is maintained and secondary reactions (if any) do not disturb this ratio. Similar constant values of 2 were found from the isomerization of *n*-hexane by Dautzenberg and Platteeuw (14) and for the hydrogenolysis of methylcyclopentane by Barron *et al.* (15), both with highly dispersed platinum catalysts. The variation in the 2-methylpentane/*n*-hexane ratio shown in Fig. 2 is in contrast to the constant ratios found previously (14-15) on platinum, and we find it difficult to avoid the conclusion that on this Co-Rh catalyst *n*-hexane is particularly sensitive to secondary reactions, and this is the reason for the rise in this ratio as the extent of reaction increases. This is in

agreement with some preliminary results on the reaction of *n*-hexane itself which will be reported subsequently (16).

Further work in progress combines physically characterizing this Co-Rh catalyst in detail and investigating the role of experimental conditions upon the isomer selectivity in paraffin hydrogenolysis and isomerization reactions. The catalyst reported here is only one member of a compositional series with cobalt and rhodium as end members which may be prepared from the corresponding bimetallic molecular cluster compounds.

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