Catalytic Activity of Lanthanide (Eu and Yb)-promoted Catalyst Systems

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Metal powders (Fe, Ni, Cu, and Ag) react readily with Eu and Yb, they dissolve in liquid ammonia, resulting in the formation of active lanthanide-promoted catalysts, the activity of which increased about 10^3—10^5 times with the lanthanide addition.

Lanthanides (rare earths) have been investigated and utilized in a wide variety of fields,[1] but less extensively in catalysis. Recently we have shown that lanthanide-catalysed reactions are of great interest and use,[2] *e.g.* lanthanides have been used as promoters for supported catalysts in synthesis gas conversion.[3] This study relates to unsupported systems, and is the first on the promotion effect of a lanthanide-metal overlayer on the adsorption and the reaction of an alkene on a transition metal surface.

Eu and Yb (purity, 99.9%), were obtained from the Shin-Etsu Chemical Co. Ltd. Ammonia (> 99.9%) produced by the Iwatani Ind. Ltd. was dried through calcium oxide and subsequently through a sodium hydroxide column. Metal powders (Fe, Ni, Cu, and Ag) were conventionally prepared by an incipient wetness technique; metal salts [$FeSO_4 \cdot 7H_2O$, $NI(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $AgNO_3$] decomposed in basic solutions, forming precipitates of hydroxides. The resulting precipitates were filtered off, washed with distilled water, dried, and reduced with hydrogen. The Brunauer–Emmett–Teller (B.E.T.) adsorption studies yielded surface area estimates for Ni, Fe, and Cu of 35, 85, and 19 $m^2\ g^{-1}$ respectively.

In a typical preparation of the lanthanide-promoted catalyst, the reduced metal powders (Fe, Ni, Cu, and Ag) were placed in liquid ammonia, the Eu or Yb powders were added in limited amounts with stirring at 195 K. It has been shown that the Eu and Yb metals dissolve in liquid ammonia to form blue solutions which are characteristic of the solvated electron.[4] Once the solution was blue, the blue colour immediately disappeared as a result of the reaction with the transition metals, the Eu or Yb powders were gradually added again. On completion of the addition the vessel was allowed to warm to room temperature and the excess ammonia was vaporized leaving a pyrophoric catalyst powder. All the operations were carried out in an atmosphere of dry argon.

The catalytic reactions were measured using a conventional

Table 1. Hydrogenation of ethylene over Eu- or Yb-promoted catalysts.[a]

Catalyst	Eu or Yb addition /atomic %	Evacuation T^b/K	Reaction T/K	Rate constant k/min^{-1} g^{-1}
Fe	—	573	293	—[c]
Eu–Fe	9.3	673	293	8.1
Yb–Fe	9.7	673	293	2.8
Yb–Fe	9.7	573	293	6.2×10^{-1}
Yb–Fe	9.7	473	293	4.1×10^{-2}
Ni	—	673	273	4.5
Eu–Ni	10.1	673	206	14.7
Yb–Ni	10.0	673	206	8.4
Cu	—	573	423	4.6×10^{-2}
Eu–Cu	3.2	673	273	7.6×10^{-1}
Yb–Cu	3.6	673	273	4.0×10^{-1}
Ag	—	423	423	—[c]
Eu–Ag	14.8	673	273	5.2×10^{-1}

[a] The reaction was conducted by admitting C_2H_4 (16 Torr) and H_2 (32 Torr). [b] 2 h. [c] The activity was zero within detection limits.

gas circulation system with a reaction space of about 300 cm^3. The catalyst was outgassed in the range 293—673 K prior to each run and was then exposed to the reacting gases.

The catalytic behaviour of the lanthanide-promoted catalysts varied markedly with the addition of Eu and Yb. The results are summarized in Table 1. The transition metals studied were used more efficiently when dosed with the lanthanide metals. The catalytic property was evaluated by the hydrogenation of ethylene as a test reaction. The first-order rate constant k was used as an index of the activity; for the Cu system, it increased by over three or four orders of magnitude with an increase in the addition of the lanthanide powders (Figure 1). The catalytic activity was not monotonically proportional to the addition of Eu or Yb, but increased abruptly with the addition of 1 to 3 atomic % lanthanide, and then progressively for further addition. This dependence of lanthanide addition on the activity indicates that the existence of any synergetic effects between the copper and lanthanide rather than individual metals constitutes active sites. This synergy is a complex effect which depends upon many factors including the electronic effect of the promoter on the catalyst and the geometrical effect. Studies on lanthanide–transition metal intermetallics have made it abundantly clear that there is electron transfer from the lanthanide to the transition metal.[5]

Details on the structure of the dosed lanthanide metal were not obtained. The lanthanide-promoted catalysts may be those in which the lanthanide spreads over the surface, dissolves in the host lattice, or aggregates to form microcrystals. The B.E.T. surface area for the copper samples was estimated as 19 m^2 g^{-1}. If the lanthanide uniformly exists in the metallic form on the copper surface, the addition of 3.2—3.6 atomic % lanthanide roughly corresponds to, at the most, monolayer or more coverage of the copper particles with Eu or Yb. Cu itself adsorbed a negligible amount of hydrogen at room temperature, but on addition of lanthanide, the amount of hydrogen adsorption by the 3.6 % Yb added-Cu sample increased to 42.1 μmol g^{-1}; the lanthanide strongly influences the catalytic activation of hydrogen.

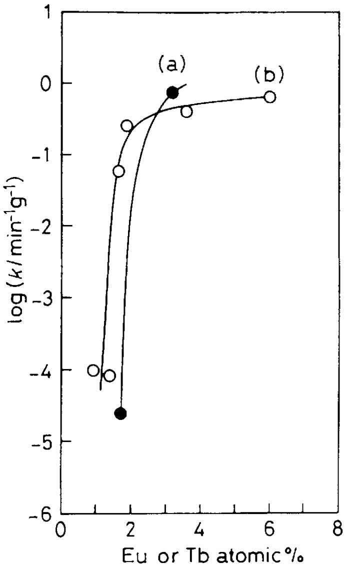

Figure 1. Hydrogenation activity (273 K) *vs.* lanthanide addition to Cu. (a) Eu; (b) Yb.

Upon the addition of lanthanide, Fe, Ni, and Ag, exhibited essentially the same behaviour as the Cu (Table 1). For the Eu- and Yb-dosed systems essentially similar dependence of the activity was observed as a function of lanthanide addition (see Table 1 and Figure 1). Comparing both systems on the basis of the same atomic fraction of lanthanide metal added to the transition metals studied, the specific activity of the Eu-dosed system was, in most cases, higher than that of the Yb-combined system.

The hydrogenation activity increased noticeably with the increase in evacuation temperature of the catalysts before each run. It increased by over three orders of magnitude with a change in temperature from 293 to 673 K. This is probably due to release of adsorbed ammonia from the catalyst surface and/or the reconstruction of surface morphology with an increase in the evacuation temperatures.

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