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Heterogeneous Selective Cyclotrimerization of Acetylene to Benzene by Lanthanide-Ti(IV) Catalysts

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In the presence of titanium halides, the oxide-supported lanthanide (Yb/SiO_2 or Yb/γ-Al_2O_3) was converted into selective cyclotrimerization catalysts of acetylene to benzene. The $TiCl_4$-treated Yb/SiO_2 catalysed trimerization of acetylene in 85% selectivity at 294 K.

Cyclotrimerization of acetylenes to arenes by transition metal (Ni, Co or Pd) complexes is well known,1) while the heterogeneously catalysed reaction has not been so much studied. Some of the works are concentrated on spectroscopic studies on Pd(111)2) or Cu(110).3) Moreover, very little is known about lanthanide-catalysed aromatization. We have studied interesting catalytic properties of lanthanides.4) In this work, we report that lanthanides highly dispersed on SiO_2 or γ-Al_2O_3 can be transformed into active acetylene trimerization catalysts when treated with $TiCl_4$.

By the use of the solubility of Eu and Yb metals in liquid NH_3,5) the oxide-supported lanthanide was prepared. SiO_2 or γ-Al_2O_3 which had been evacuated at 673 K or 573 K, respectively, was impregnated with the solution of dissolved Eu or Yb in liquid NH_3 at 195 K. The solution was at first blue, but the blue color immediately disappeared as a result of the deposition of lanthanide on the oxide. On completion of the deposition, the vessel was allowed to warm to room temperature and the excess NH_3 was vaporized. XRD of Yb/SiO_2 showed negligible changes before and after the deposition; thus, the lanthanide probably exists in a high dispersion state on the oxide surface. Even if Yb uniformly exists in the metallic form on SiO_2 (170 $m^2 \cdot g^{-1}$), the deposition of 14.7 wt%-Yb doesn't amount to monolayer coverage of SiO_2 with Yb. However, some questions remain as to the reaction between the oxide and lanthanide metals. Further, the oxide-supported lanthanide was evacuated at 373 K for 1.5 h, followed by treatment with solutions of $TiCl_4$ (or $TiBr_4$) in refluxing hexane. The catalysts thus prepared were dried *in vacuo* at 294 K. The reaction was examined using a conventional gas circulation system (367 cm^3).

The $TiCl_4$-treated Yb/SiO_2 (Yb/SiO_2-$TiCl_4$) effectively catalysed the cyclotrimerization of acetylene to benzene at 283-373 K although the individual component exhibited negligible activities (Table 1). The product detected in the gas phase was only benzene. However, the decrease in acetylene in the gas phase didn't always correspond to the conversion into benzene; oligomerization reactions would occur to some extent. For the reaction at higher temperatures, the catalyst was irreversibly deactivated and the selectivity was very low. It was found that acetylene was selectively trimerized to benzene under mild conditions. Heterogeneously catalysed aromatization reactions usually occur at much higher temperatures.[6] The activity of Yb/SiO_2-$TiCl_4$ was generally high compared to that of Eu/SiO_2-$TiCl_4$. When methylacetylene was used instead of acetylene, mixed trimethylbenzenes (1,3,5- and 1,2,4-trimethylbenzene) were selectively produced at 294 K; 58% selectivity of aromatization was recorded.

The cyclotrimerization activity was dependent upon the addition amounts of $TiCl_4$. The activity increased with the addition of $TiCl_4$ to Yb/SiO_2, passed through a maximum and decreased with further addition. The amount of lanthanide loading on the oxide was also important in determining catalytic behavior. The catalyst system requires careful optimization of the ratio of lanthanide and $TiCl_4$ to avoid polymer formation and thereby improves yield of benzene.

Table 1. Results on the cyclotrimerization of alkyne[a]

Alkyne	Catalyst[b]		Rate[d]	Selectivity[e]
	Lanthanide	Ti(IV)/mmol[c]	mmol·min^{-1}·g^{-1}	%
C_2H_2	14.7 wt%-Yb/SiO_2	-	-	-
C_2H_2	0 wt%-Yb/SiO_2	$TiCl_4$/0.5	-	-
C_2H_2	14.7 wt%-Yb/SiO_2	$TiCl_4$/0.1	3.3×10^{-2}	59
C_2H_2	14.7 wt%-Yb/SiO_2	$TiCl_4$/0.5	2.2×10^{-1}	85
C_2H_2	14.7 wt%-Yb/SiO_2	$TiCl_4$/0.7	7.0×10^{-2}	23
C_2H_2	14.7 wt%-Yb/γ-Al_2O_3	$TiCl_4$/0.5	1.0×10^{-1}[f]	70
C_2H_2	14.7 wt%-Yb/SiO_2	$TiBr_4$/0.5	1.3×10^{-2}	2
C_2H_2	8.0 wt%-Yb/SiO_2	$TiCl_4$/0.5	1.0×10^{-3}	30
C_3H_4	14.7 wt%-Yb/SiO_2	$TiCl_4$/0.5	2.9×10^{-2}	58

a) The reaction was carried out by admitting alkyne (29 Torr) at 294 K.
b) The catalyst was evacuated at 573 K for 2 h before each run.
c) The amount of Ti(IV) added is expressed in units per gram of supported-lanthanide. d) Rate of alkyne decrease. e) Selectivity of arenes.
f) The catalyst was evacuated at 673 K for 2 h.

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