

Cyclization of Ethyne and Propyne over Lanthanide Catalysts Deposited from Eu or Yb Metal Solutions in Liquid Ammonia

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Europium and ytterbium catalysts separated on active carbon from a solution of lanthanide metals dissolved in liquid ammonia were found to be effective for oligomerization of alkynes. Selective cyclic dimerization and trimerization of propyne and ethyne to cyclohexadiene and benzene occurred during the oligomerization, respectively, in which the active catalysts were characterized as lanthanide imides induced by the thermal treatment.

Recently there has been a growing interest in lanthanides and their derivatives for potential synthetic and catalytic activity. It has been shown that the use of dissolution of lanthanide metals (Ln = Eu and Yb) in liquid ammonia enables the preparation of novel lanthanide-containing catalyst materials which exhibit specific catalytic properties for hydrogenation.¹ In this study, we report that the catalysts prepared by the deposition of lanthanides on active carbon from a solution of Eu or Yb metals dissolved in liquid ammonia are active for the selective cyclization of alkynes: the conversion of ethyne and propyne into

benzene and cyclohexadiene, respectively. There have been few studies published of catalytic cyclization of propyne to cyclohexadiene on lanthanides to the best of our knowledge. Selective cyclization is also of great potential synthetic importance.

In a typical preparation of the catalysts, the active carbon (designated hereafter as AC; Nakarai Chemicals Ltd.) which had been previously subjected to evacuation at 873 K for 20 h was placed in a Schlenk tube and then ammonia of about 20 cm³ was liquefied. Eu or Yb (99.9 %; Shin-Etsu Chemical Co. Ltd.) in limited amounts was added to the AC powder suspended in liquid ammonia with stirring at 198 K. The lanthanide metals immediately dissolved in liquid ammonia to form a homogeneous solution containing solvated electrons with an intense blue color,² which gradually faded as a result of the occurrence of lanthanide deposition on AC. On completion of the deposition, the excess ammonia was removed under vacuum at 198 K leaving AC-supported lanthanide catalysts (Ln/AC). The content of lanthanides in the catalysts was represented by the fraction of wt%. Ln/AC was pretreated at 298–1273 K *in vacuo* for 2 h

Table 1. Reactions of ethyne and propyne over Ln/AC catalysts at 453 K^a

Propyne							
Catalyst ^b	Evacuation temp./K ^c	Propyne conv./% ^d	Cyclization selectivity/%	Product composition /% ^e			
				1,3-C ₆ H ₈	1,4-C ₆ H ₈	Other dimers	Higher oligomers
60% Eu/AC	573	43	27	0	27	3	70
30% Yb/AC	623	97	40	7	33	0	60
	773	44	11	7	4	0	89
	1273	23	10	10	0	0	90
60% Yb/AC	453	67	60	12	48	6	34
	623	78	44	2	42	16	40
	773	51	37	2	35	0	63
	1123	34	5	0	5	0	95
Yb amide	298	0					
	503	14	23	2	21	0	77
	1073	0					
Eu amide	298	0					
	503	15	61	9	52	12	27
Yb	523	0					

Ethyne					
Catalyst ^b	Evacuation temp./K ^c	Ethyne conv./% ^d	Cyclization selectivity/%	Product composition /% ^e	
				C ₆ H ₆	Higher oligomers
30% Eu/AC	773	65	1	1	99
60% Yb/AC	773	80	6	6	94
	973	74	1	1	99
	1273	39	0	0	100
Yb	523	0			

^a The reaction was carried out with 30 Torr of alkyne. ^b Catalyst = 100 mg. ^c For 2 h. ^d After 3 h.

^e Composition of oligomerization products.

before use. The catalytic reactions were carried out in a gas-recirculation reactor (*ca.* 140 cm³) and the reacting gas was analyzed by a Shimadzu GC-MS (QP2000GF).

We have carried out reactions at 453 K with ethyne and propyne, using Ln/AC catalysts which are differently activated (Table 1). The lanthanide catalysts were very active for oligomer formation; in particular the selective cyclization of propyne to cyclohexadienes occurred. Cyclohexa-1,3-diene and -1,4-diene were observed as main dimer products besides higher oligomers. Selectivities of 60% for cyclohexadiene were recorded in 60% Yb/AC-catalyzed reactions. Chain dimer products other than cyclohexadiene were rarely observed. The Ln/AC catalysts were also active for the isomerization of propyne to allene, leading to the speculations of allene intermediates. The preferential isomerization of propyne to allene with subsequent coupling of adsorbed precursors is expected. It has been shown that allene is catalytically converted into a mixture of isomeric trimers, tetramers and higher oligomers by a nickel complex.³ Oligomerization of alkynes is explained in terms of a mechanism attributed to recent work by Cant⁴ and described in some details by Bond.⁵ However, scarcely any studies have been reported with the cyclization of propyne to cyclohexadiene.

When ethyne was used as a reactant, the trimerization occurred along with the rapid formation of higher oligomers. Benzene was observed as a main product in the gas-phase, but its selectivity was relatively low (Table 1). However, Ln/AC-catalyzed propyne reaction yielded no trimerization products. Eu/AC and Yb/AC showed almost similar catalytic behavior.

The catalytic behavior of Ln/AC remarkably depended upon the thermal pretreatment *in vacuo*. The evacuation treatment of Ln/AC at elevated temperatures (298–1273 K) for 2 h, before the reaction, strongly affected the catalytic properties. As shown in Table 1, the activity and selectivity for propyne dimerization and ethyne trimerization showed a tendency to decrease with increasing the evacuation temperatures. As shown in Figure 1, XRD of 60 wt% Yb/AC revealed the existence of metallic ytterbium in the cubic structure, and a further increase in the pretreatment temperature from 298 to 623 K resulted in the occurrence of crystallization to a significant extent. However, the lanthanide on AC began to be converted into the nitride (YbN) when subjected to the thermal treatment above 773 K. It is accepted that thermal decomposition products of liquid ammonia solutions of Eu and Yb metals are finally the nitride (EuN and YbN) through amides or imides.^{6,7} For ytterbium and europium introduced into Y-zeolite by impregnation from the lanthanide metals dissolved in liquid ammonia, it has been claimed that the imide, such as EuNH, formed by the thermal treatment under vacuum is one of the catalytically active species.⁸ However, there was no indication of lanthanide amides or imides in XRD of the present catalyst systems.

For comparison, the Yb metal catalysts prepared by the metal vapor technique⁹ exhibited negligible activity for the cyclization and oligomerization of acetylenic compounds. Furthermore, Eu amide and Yb amide prepared according to ref. 7 were a mixture of divalent and trivalent states and they were hardly active. However, upon the thermal treatment around 503 K which led to the formation of lanthanide imides,⁶ the activity and selectivity for propyne cyclization appeared and further treatment at 1073 K

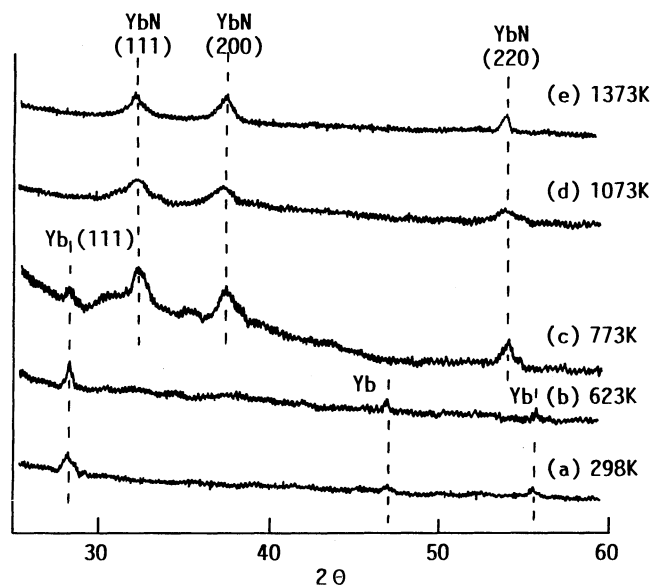


Figure 1. XRD of 60% Yb/AC
60% Yb/AC was evacuated at each temperature for 2 h.

resulted in complete deactivation with conversion of the catalyst into nitride (Table 1). Therefore, it is highly probable that the lanthanides in the form of imide rather than metal and nitride, which were actually detected by XRD (Figure 1), are active species for the present cyclization reactions. Such species formed on Ln/AC seem to decompose with raising the evacuation temperatures above 773 K, resulting in a decrease in activity and selectivity for the cyclization.

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References and Notes

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