

## Selective Dimerization of Ethene over Lanthanide Catalysts Deposited from Eu or Yb Metal Solutions in Liquid Ammonia

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Europium and ytterbium catalysts obtained by impregnation of active carbon with lanthanide metal (Eu and Yb) solutions in liquid ammonia were found to be active for the dimerization of ethene. Ethene was selectively dimerized at 423–473 K to yield butene isomers with selectivity of 10–62%. The active catalysts were characterized as lanthanide nitride formed by the thermal decomposition of its amide.

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 catalysts which exhibit specific properties for various reactions.<sup>1</sup> In this study, we report that the catalysts prepared by impregnation of active carbon with solutions of Eu or Yb metals dissolved in liquid ammonia are active for the highly selective dimerization of ethene. There have been few studies published of catalytic dimerization of ethene to butenes on lanthanides to the best of our knowledge. Selective dimerization of alkenes is also of great potential synthetic and industrial importance.<sup>2</sup>

Ammonia gas was purified through a calcium oxide column and subsequently through a sodium hydroxide column. Active carbon (designated hereafter as AC) obtained from Nacalai Tesque Inc. was evacuated at 873 K for 18 h and subsequently treated with hydrogen at 673 K. In a typical preparation of AC-supported lanthanide catalysts (Ln/AC) with Ln loading of 10–20 wt%, in a 50 cm<sup>3</sup> stainless steel reactor were placed Eu or Yb metals (0.12–0.24 g; 99.9%; Santoku Co.) and AC (1.2 g) under an atmosphere of dry nitrogen. The reactor was briefly evacuated, cooled by a dry ice/methanol bath, and then, about 3000 cm<sup>3</sup> of purified ammonia gas was liquefied. The Eu and Yb metal readily dissolved in liquid ammonia to yield a homogeneous solution containing the ammoniated electrons,<sup>3</sup> with which AC was impregnated. Upon stirring at 293 K for 6–10 h, the dissolved lanthanide was deposited in the form of amide on AC. Ammonia was subsequently removed from the reactor leaving Ln/AC. Ln/MnO, Ln/TiO<sub>2</sub> and Ln/ZrO<sub>2</sub> were similarly prepared. The catalytic reactions were carried out in a gas-recirculation reactor with a fixed volume of ca. 364 cm<sup>3</sup>.

Ethene was effectively dimerized into mixed n-butene isomers when brought into contact with various lanthanide catalysts (Ln/AC, Ln/MnO, Ln/TiO<sub>2</sub> and Ln/ZrO<sub>2</sub>) at 473 K. The lanthanide catalysts exhibited activity for ethene oligomerization with selectivity toward butene formation. Yb/AC and Eu/AC showed similar catalytic behavior, and especially Yb/AC was excellent in activity and selectivity for butene formation compared to other catalysts. The lanthanide for Ln/AC was

highly dispersed, but the reason why the catalysis of Yb systems was superior to that of Eu systems is unknown.

The dimerization of ethene on Yb/AC began from reaction temperatures near 373 K. Time courses of 10% Yb/AC-catalyzed ethene dimerization at 473 K were shown in Figure 1. The consumption of the ethene reactant did not necessarily agree with the amounts of the butene products. No products other than butenes were detected by gas chromatography; thus the oligomerization to products with higher molecular weights occurs at the same time. Accumulation of such oligomerized deposits on the catalysts would probably result in gradual deactivation of Yb/AC with reaction time as shown in Figure 1. In the range where the steady formation of butenes was observed, the butene selectivity evaluated by percentage of the amounts of actually formed butenes to the amounts of butenes calculated from ethene consumed remained unchanged at approximately 62% during the reaction. Yb/AC preferentially yielded but-2-ene (90%) with a trans/cis ratio of about 2, being close to equilibrium composition of butenes at 473 K. The initial rates of Ln/AC-catalyzed dimerization were proportional to the first power of the ethene pressure (10–200 Torr; 1 Torr=133.322 Pa).

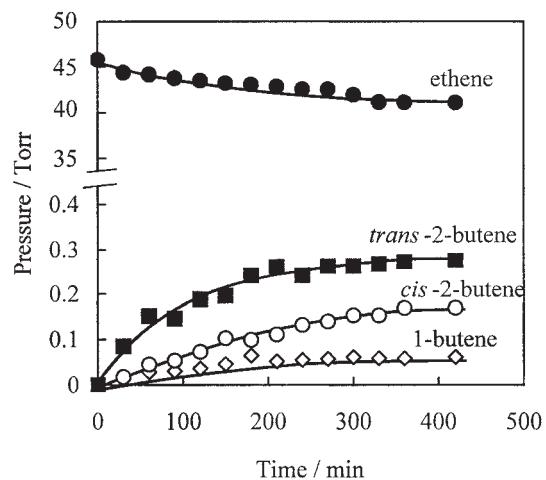
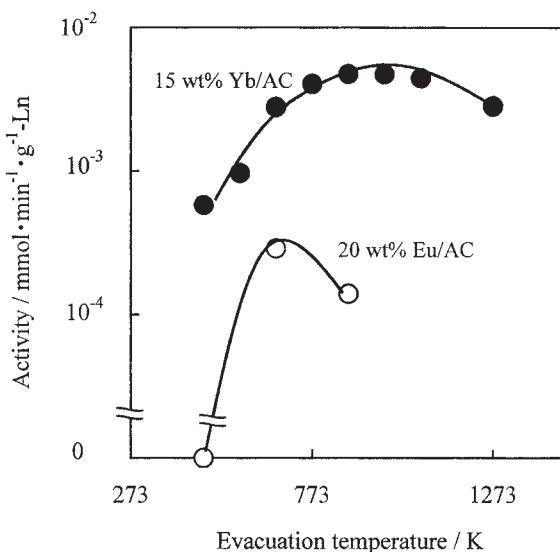


Figure 1. Time courses of 10% Yb/AC-catalyzed ethene dimerization at 473 K.

The catalytic properties of 20% Eu/AC and 15% Yb/AC for the dimerization strongly depended upon thermal pretreatment with evacuation (Figure 2). The activity and selectivity for Yb/AC-catalyzed ethene dimerization increased with increasing evacuation temperatures and passed through a maximum around 973 K. As shown in Figure 2, Eu/AC showed a maximal activity when evacuated around 673 K. In XRD of 20% Eu/AC and 15%



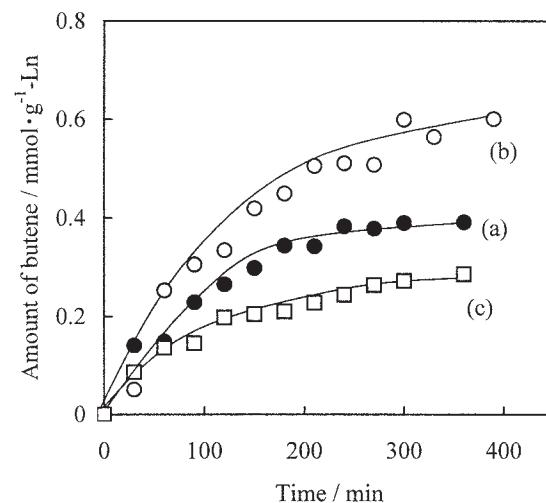
**Figure 2.** Effects of thermal pretreatment of 20% Eu/AC and 15% Yb/AC on the activity for ethene dimerization.

Yb/AC thus treated, no diffraction peaks of lanthanides were detected owing to high dispersion of the lanthanide on AC. In Ln/AC prepared by the impregnation method using liquid ammonia solutions of Eu or Yb metal, the lanthanide is known to exist exclusively in the form of amides.<sup>4,5</sup> Moreover, it has been shown that europium amide and ytterbium amide are thermally decomposed to nitride (LnN) through imide (LnNH) when subjected to the thermal treatment above 573 and 773 K, respectively.<sup>5,6</sup> Lanthanides introduced into Y-zeolite by impregnation from Eu or Yb metal solutions in liquid ammonia are also converted into imide and nitride by evacuation at elevated temperatures.<sup>7</sup> The catalysis of EuN and YbN prepared separately by the thermal decomposition of the lanthanide amides, Eu(NH<sub>2</sub>)<sub>2</sub> and Yb(NH<sub>2</sub>)<sub>3</sub>, was examined for comparison, respectively. YbN decomposed at 973 K exhibited the highest activity for the dimerization with butene selectivity of 16%, while EuN decomposed at 673 K was also active with selectivity of 4%. Their composition of butene products was also similar to that for Eu/AC and Yb/AC. Judging from these results, it seems quite certain that the lanthanide nitride formed on AC upon thermal treatment of Ln/AC is catalytically effective for the dimerization of ethane.

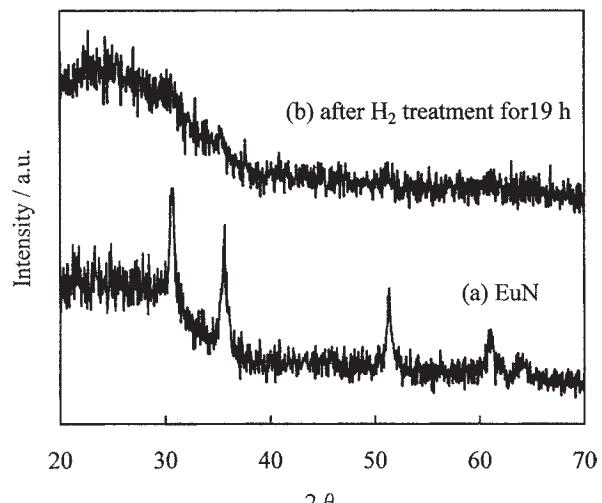
An interesting feature of Ln/AC is that the activity and selectivity were greatly improved upon treating with hydrogen as shown in Figure 3. The activity for butene formation increased approximately two times when 15% Yb/AC evacuated at 973 K was additionally treated with hydrogen of 50 Torr for 1 h at room temperature, while the selectivity for butenes rose from 25 to 41%. 20% Eu/AC evacuated at 673 K showed about 2-fold selectivity when similarly treated with hydrogen. However, when Ln/AC was excessively treated with hydrogen for a long time, the activity oppositely fell to a considerable extent. This is likely due to that the catalytically active nitride was decomposed as evidenced by XRD of EuN (Figure 4).

## References

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**Figure 3.** Effects of H<sub>2</sub> treatment of 15% Yb/AC on the activity for ethene dimerization. The catalyst was treated with hydrogen of 50 Torr for (a) 0 h, (b) 1 h and (c) 21 h.



**Figure 4.** XRD of EuN, (a) obtained upon evacuation at 673 K and (b) treated with H<sub>2</sub>.

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