

## Highly Selective Hydrogenation of Benzene to Cyclohexene catalysed by a SiO<sub>2</sub>- or Al<sub>2</sub>O<sub>3</sub>-Immobilized Lanthanide Catalyst

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Ytterbium catalysts immobilized on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, which are formed by the reaction of the support with the lanthanide dissolved in liquid ammonia, are a new catalytic material for the partial hydrogenation of benzene to cyclohexene with extremely high selectivity of 96–100%.

Synthetically and industrially it is of great interest to reduce partially benzene to cyclohexene. A number of heterogeneous catalyst systems (the best being ruthenium-based) have been reported for the partial hydrogenation of benzene.<sup>1</sup> However, despite strenuous attempts to optimise the catalysts, high selectivities towards cyclohexene have not been obtained.

Recently, we have developed methods for the preparation of a new catalytic materials containing lanthanides and have demonstrated that they exhibit specific catalytic behaviour.<sup>2</sup> In this communication, we report unexpected and interesting properties of this class of catalysts prepared by the immobilization of lanthanide species on the surface of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> for the selective gas-phase hydrogenation of benzene to cyclohexene.

The lanthanide catalysts used here require a particular preparation technique by the use of dissolution of lanthanide metals in liquid ammonia.<sup>†</sup> Following preparation of the

catalyst, the gas-phase hydrogenation of benzene (20 Torr, 1 Torr = 133.322 Pa) with hydrogen (120 Torr) was carried out over Yb/SiO<sub>2</sub> at 298 K using a Pyrex gas-circulation system (Table 1). Although benzene is one of the most difficult of all unsaturated compounds to hydrogenate, Yb/SiO<sub>2</sub> could readily reduce benzene to cyclohexene even at 298 K. The products were mostly cyclohexene, containing small amounts of cyclohexane. As shown in Table 1, a very important characteristic of the lanthanide catalyst immobilized on the support is that the selectivity for cyclohexene attains 96–100% and is extremely high compared to other reported catalysts.<sup>1</sup>

**Table 1** Gas-phase hydrogenation over SiO<sub>2</sub>- or Al<sub>2</sub>O<sub>3</sub>-immobilized lanthanide catalysts at 298 K<sup>a</sup>

Entry	Catalyst	Reactant	Activity <sup>b</sup>	Selectivity <sup>c</sup> (%)
1	15%-Yb/SiO <sub>2</sub>	Benzene	$1.8 \times 10^{-4}$	100
2 <sup>d</sup>	15%-Yb/SiO <sub>2</sub>	Cyclohexene	— <sup>e</sup>	—
3 <sup>d</sup>	15%-Yb/SiO <sub>2</sub>	Cyclohexa-1,3-diene	$6.9 \times 10^{-4}$	100
4	20%-Yb/SiO <sub>2</sub>	Benzene	$1.9 \times 10^{-4}$	96
5	24%-Yb/SiO <sub>2</sub>	Benzene	$3.4 \times 10^{-4}$	97
6	13%-Eu/SiO <sub>2</sub>	Benzene	— <sup>e</sup>	—
7	16%-Yb/Al <sub>2</sub> O <sub>3</sub>	Benzene	$2.2 \times 10^{-4}$	96
8	22%-Yb/Al <sub>2</sub> O <sub>3</sub>	Benzene	$3.4 \times 10^{-4}$	99

<sup>a</sup> Prior to the reaction the catalysts (ca. 100 mg) were evacuated at 298 K and the reacting gases were admitted; reactant = 20 Torr, H<sub>2</sub> = 120 Torr. <sup>b</sup> mmol of reactant converted min<sup>-1</sup> g cat<sup>-1</sup>. <sup>c</sup> C<sub>6</sub>H<sub>10</sub>/(C<sub>6</sub>H<sub>10</sub> + C<sub>6</sub>H<sub>12</sub>) × 100. <sup>d</sup> The catalysts, previously evacuated at 373 K, brought into contact with the reacting gases; reactant = 20 Torr, H<sub>2</sub> = 40 Torr. <sup>e</sup> The activity was almost zero within detection limits.

<sup>†</sup> Silica gel (Degussa Aerosil 380) and alumina (Reference Catalyst of the Catalysis Society of Japan<sup>3</sup>; ALO-2) were used as a support. In a typical preparation of 15 wt% Yb/SiO<sub>2</sub>, SiO<sub>2</sub>, (0.8 g) which had been previously evacuated at 1073 K for 10 h was placed in a Schlenk tube, in which purified ammonia was liquefied at 198 K. Yb (0.14 g) (99.9%; Shin-Etsu Chemical Co. Ltd.) was added to the SiO<sub>2</sub> powders suspended in liquid ammonia (ca. 20 cm<sup>3</sup>) with vigorous stirring at 198 K. Upon dissolution of the lanthanide metal in liquid ammonia, a blue homogeneous solution was formed, characteristic of divalent metal cations and solvated electrons.<sup>4</sup> The blue colour of the solution faded gradually with stirring as a result of the reaction of the dissolved lanthanide metal with SiO<sub>2</sub>. On disappearance of the blue colour, the vessel was allowed to warm to room temperature and the excess ammonia was pumped off leaving active 15%-Yb/SiO<sub>2</sub> catalysts. All sample preparation steps were carried out in an atmosphere of dry argon without exposure to air, otherwise the catalysts became unreactive.

A further useful property of Yb/SiO<sub>2</sub> is that the conversion of benzene increased, but the high selectivity for cyclohexene remained almost unchanged. However, Eu/SiO<sub>2</sub> showed negligible activity at 298 K.

The surface of silica gel consists of reactive silanol groups ( $\equiv\text{Si}-\text{OH}$ ). We have established from extensive Fourier-transform IR (FTIR) studies that when the silica gel is brought into contact with the solution of ytterbium dissolved in liquid ammonia, the hydroxy groups on the surface react preferentially with the dissolved lanthanide to form  $\equiv\text{Si}-\text{O}-\text{Yb}-\text{NH}_2$ .<sup>2,5</sup> An interesting feature of the lanthanide catalysts grafted thus onto SiO<sub>2</sub> is that they show negligible or very low reducing power for monoenes (ethene, propene and butene), in marked contrast to their high reactivity for conjugated dienes (buta-1,3-diene and penta-1,3-diene).<sup>2</sup> Included in Table 1 for comparison are the results on the hydrogenation of cyclohexene and cyclohexa-1,3-diene. Cyclohexadiene was readily reduced to cyclohexene with almost 100% selectivity at 298 K, whereas cyclohexene was virtually inactive for Yb/SiO<sub>2</sub>. This is a reason why the selectivity of the present catalyst systems is extremely high. In spite of thermodynamic disadvantages ( $\Delta G^\circ$  at 298 K:  $-23 \text{ kJ mol}^{-1}$  for benzene to cyclohexene and  $-98 \text{ kJ mol}^{-1}$  for benzene to cyclohexane) there is a strong tendency for the reaction over the lanthanide catalysts to stop at the partially hydrogenated intermediate, rather than to proceed all the way to cyclohexane as over conventional catalysts.

The surface density of hydroxyl group on SiO<sub>2</sub> as a function of the evacuation temperature has been thoroughly investigated.<sup>6</sup> Hence Yb/SiO<sub>2</sub> with varied levels of the grafted lanthanide (15, 20 and 24%) could be prepared using SiO<sub>2</sub> evacuated at 1073, 923 and 773 K, respectively.† For these

Yb/SiO<sub>2</sub> catalysts the rate of hydrogenation of benzene increased with an increase in loadings of lanthanide. However, the specific rates expressed as turnover frequencies in terms of molecules of cyclohexene formed per site per second are almost independent of the quantities of loadings of lanthanide and the support types used. Alumina, as well as silica, has surface hydroxy groups. The grafting of lanthanide onto Al<sub>2</sub>O<sub>3</sub> similarly led to specific catalytic activity for the partial hydrogenation of benzene to cyclohexene (Table 1). Upon thermal treatment of the catalysts above 575 K, the activity of hydrogenation disappeared and simultaneously IR spectra showed the decomposition of the SiO<sub>2</sub>- or Al<sub>2</sub>O<sub>3</sub>-immobilized lanthanide species.

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† From the surface density of the hydroxy group (about 1.5, 2.2 and 2.8 OH nm<sup>-2</sup>)<sup>6</sup> and the surface area of SiO<sub>2</sub> was determined the mass of the lanthanide metal grafted onto the support considering a lanthanide metal to hydroxy group ratio of 1 : 1 in the surface complex.