Selective Hydrogenation of Conjugated and Nonconjugated Double Bonds using Lanthanides Immobilized on SiO_2

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Europium or ytterbium catalysts immobilized on SiO_2 (Eu/SiO_2 and Yb/SiO_2) formed by the reaction of SiO_2 with the lanthanides dissolved in liquid ammonia, which Fourier-transform IR studies showed have the structure $\equiv Si{-}O{-}M{-}NH_2$ (M = Eu or Yb), showed selective hydrogenation properties, discriminating between conjugated and nonconjugated dienes.

Heterogeneous hydrogenation of dienes with discrimination between conjugated and nonconjugated C=C double bonds has been difficult for catalytic chemists to achieve. Moore *et al.* have reported that when molybdenum and nickel sulphide catalysts are used the reaction only takes place with conjugated systems.[1] In the case of solid base catalysts, selective hydrogenation of conjugated dienes occurs.[2] We now report the high activity and selectivity shown by lanthanides immobilized on SiO_2 (Eu/SiO_2 and Yb/SiO_2) for the hydrogenation of conjugated and nonconjugated dienes. We also provide information on the active species evaluated by Fourier transform (FT) IR studies on our catalyst systems.

The lanthanide catalysts used require a particular preparation method. SiO_2 ($380\ m^2\ g^{-1}$; Degussa Aerosil) which had been previously evacuated at 1073 K for 10 h was placed in a Schlenk reactor flushed thoroughly with dry argon. Eu (0.15 g) or Yb (0.17 g) (99.9%; Shin-Etsu Chemcial Co. Ltd.) was added to the SiO_2 powder (1.0 g) suspended in liquid ammonia (*ca.* 20 cm^3) with vigorous stirring at 198 K. Upon dissolution of the lanthanide metals in the liquid ammonia, a blue homogeneous solution was formed, characteristic of divalent metal cations and solvated electrons.[3] The blue colour gradually disappeared as a result of the reaction of the dissolved lanthanide metal with SiO_2. On disappearance of the blue colour, the vessel was allowed to warm to room temperature and the excess of ammonia was pumped off leaving active Eu/SiO_2 and Yb/SiO_2 catalysts. All sample preparation steps were carried out in an atmosphere of dry argon, otherwise the catalysts became unreactive. The catalytic reactions were carried out using a Pyrex gas-circulation system (365 cm^3). Propene, but-1-ene, buta-1,3-diene, isoprene, penta-1,3-diene, penta-1,4-diene, hexa-1,4-diene, cyclohexa-1,3-diene and cyclohexa-1,4-diene were of research purity and further purified by degassing, followed by triple distillation. IR spectra were recorded on a JASCO FT-IR 7000 spectrometer. Samples for IR studies were prepared by the above method. To a solution of Eu or Yb in liquid ammonia was added an IR disc of SiO_2, which had been evacuated at 973 K, treated in an oxygen flow at 723 K, and again evacuated at 723 K for 0.5 h.

The results for various hydrogenations using Eu/SiO_2 and Yb/SiO_2 are summarized in Table 1. These hydrogenations show interesting features, of use for catalytic reactions. First, the lanthanide on SiO_2 discriminated between conjugated and

Table 1 Hydrogenation of various compounds over Eu/SiO_2 and Yb/SiO_2

Catalyst[a]	Reactant[b]	Activity[c] at 298 K	Product (%)[d]
Eu/SiO_2	But-1-ene	—[e]	—
	Buta-1,3-diene	5.9×10^{-4}	But-1-ene (51), (*Z*)-but-2-ene (49), (*E*)-but-2-ene (trace)
	Penta-1,4-diene	—[e]	—
Yb/SiO_2	Propene	5.5×10^{-5}	Propane (100)
	But-1-ene	4.4×10^{-5}	Butane (100)
	Buta-1,3-diene	6.5×10^{-2}	But-1-ene (24), (*Z*)-but-2-ene (57), (*E*)-but-2-ene (trace)
	Isoprene	4.3×10^{-2}	3-Methylbut-1-ene (18), 2-methylbut-1-ene (27), 2-methylbut-2-ene (55)
	Penta-1,3-diene	8.7×10^{-3}	Pent-1-ene (17), pent-2-ene (83)
	Penta-1,4-diene	—[e]	—
	Hexa-1,4-diene	—[e]	—
Yb[f]	Propene	1.1×10^{-3} at (323 K)	Propane (100)
	Penta-1,4-diene	3.5×10^{-5}	Pentane (20), pent-1-ene (80)

[a] Prior to the reaction the catalyst (*ca.* 50 mg) was evacuated at 373 K for 2 h. [b] *P*(Reactant) 20 Torr, *P*(H_2) 40 Torr. [c] mmol of reactant converted min^{-1} (g lanthanide)$^{-1}$. [d] Selectivity in parentheses. [e] The activity was almost zero within detection limits. [f] See ref. 4.

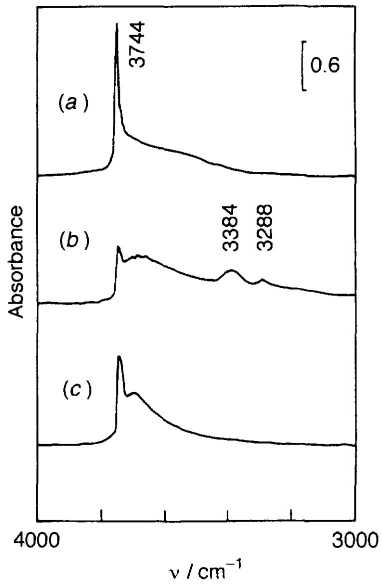

Fig. 1 IR spectra of (*a*) SiO_2, (*b*) sample after the reaction of (*a*) with dissolved Yb in liquid ammonia (Yb/SiO_2), and (*c*) sample after evacuation of (*b*) at 573 K

nonconjugated double bonds. Thus, buta-1,3-diene, isoprene, penta-1,3-diene and cyclohexa-1,3-diene were readily reduced to the monoenes at 298 K, with almost 100% selectivity, whereas penta-1,4-diene and hexa-1,4-diene remained unchanged. For cyclohexa-1,4-diene, preferential isomerization to cyclohexa-1,3-diene with subsequent hydrogenation occurred. A further useful property of the present catalysts is that they showed negligible or very low reducing power for monoenes (propene and but-1-ene), in marked contrast to their reactivity with dienes. Eu/SiO_2 and Yb/SiO_2 showed similar catalytic behaviour, but the activity of Yb/SiO_2 was much higher than that of Eu/SiO_2. For all the reactions studied, SiO_2 itself showed negligible activity. As shown in Table 1 for comparison, the lanthanide metal catalyst prepared by the metal vapour technique was active for the hydrogenation of monoenes and dienes,[4] and did not exhibit such a specific selectivity for conjugated and nonconjugated dienes. Thus grafting the lanthanide onto SiO_2 led to specific catalytic activity.

The nature of the supported lanthanide species has been investigated by FT IR studies; preliminary results indicate the formation of $\equiv$Si–O–M–NH_2 species (M = Eu or Yb) from the following observations. As shown in Fig. 1, the vibration band at 3744 cm^{-1} of SiO_2 which is assigned to free hydroxy groups[5] decreased immediately upon contact with the lanthanide. New absorptions were simultaneously observed at 3384, 3288 and 1552 cm^{-1}, which could be assigned to the NH_2 species bound to the lanthanide by comparison with published data.[6] In the absence of the lanthanide on SiO_2, these bands did not appear at all. It is accepted that on evacuation of SiO_2 at *ca.* 1023 K only free, unpaired $\equiv$Si–OH groups are present.[5] Considering the surface density of hydroxy group (about 1.5 OH nm^{-2})[7] and the surface area of SiO_2 used, the amounts of lanthanide added here roughly correspond to the total amount of hydroxy groups present on the surface of SiO_2 by assuming a lanthanide metal to hydroxy group ratio of 1 : 1 in the surface complex. Thus the interpretation of these data gives an indication that the dissolved lanthanide in liquid ammonia reacts with the surface hydroxy groups of SiO_2 to form $\equiv$Si–O–M–NH_2. This was also confirmed by the reaction of triphenylsilanol with dissolved lanthanides in liquid ammonia, which was carried out as a model reaction. However, upon thermal treatment above 573 K IR spectra showed the decomposition of the SiO_2-grafted lanthanide species (Fig. 1); $\equiv$Si–OH is probably regenerated and the amide is converted to nitride.[8] The catalyst was found to be completely deactivated at the same time. For the present hydrogenations the active species are those in which the lanthanide is grafted onto the surface hydroxy groups on SiO_2.

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References

1 R. J. Moore, R. A. Trimble and B. S. Greensfelder, *J. Am. Chem. Soc.*, 1952, **74**, 373.

2 S. Malinowski and M. Marczewski, in *Catalysis* (Specialist Periodical Report), ed. G. C. Bond and G. Webb, Royal Society of Chemistry, Cambridge, vol. 8, 1989, p. 107; H. Pines and W. M. Stalick, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press, New York, 1977.

3 W. J. Peer and J. J. Lagowski, *J. Phys. Chem.*, 1980, **84**, 1110; J. C. Thompson, *Electrons in Liquid Ammonia*, Clarendon Press, Oxford, 1976.

4 H. Imamura, K. Kitajima and S. Tsuchiya, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1647.

5 R. K. Iler, *The Chemistry of Silica Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley, New York, 1979.

6 D. J. Hewkin and W. P. Griffith, *J. Chem. Soc. (A)*, 1966, 472.

7 L. T. Zhuravlev, *Langmuir*, 1987, **3**, 316.

8 K. Howell and L. L. Pytlewski, *J. Less-Common Met.*, 1969, **19**, 399.