Effect of Reduction and Oxidation on the Activity of Ruthenium/Titania Catalysts for n-Butane Hydrogenolysis

Geoffrey C. Bond and Xu Yide†
Department of Chemistry, Brunel University, Uxbridge UB8 3PH, U.K.

The activity of Ru/TiO_2 catalysts for n-butane hydrogenolysis is greatly increased by oxidation at 433 K after reduction at 758 or 893 K; strong metal–support interaction is then easily effected by a second reduction at these temperatures.

One of the more curious features of the strong metal–support interaction (SMSI) induced by high temperature reduction (773 K) of TiO_2-supported metal precursors[1] is that the susceptibility of different metals to changes in their activity for structure-sensitive reactions appears to vary greatly. One report[2] states that after high temperature reduction Ru/TiO_2 has the same activity for ethane hydrogenolysis as Ru/SiO_2, while Pt/TiO_2 is more than 500 times less active than Pt/SiO_2. However in another report[3] Ru/TiO_2 after high temperature reduction is said to be 5000 times less active than Ru/SiO_2. In seeking to explain this discrepancy we have found that the activity of Ru/TiO_2 is sensitive to variations in its pretreatment.

Catalysts composed of 1% and 5% Ru/TiO_2 were prepared by impregnating Degussa P-25 TiO_2 with $RuCl_3$ solution, followed by drying at 400 K. Rates of n-butane hydrogenolysis measured at 433 K in a continuous flow system following various reduction and oxidation treatments are shown in Table 1. Each sample was first reduced at either 623, 758, or 693 K for 16 h and its activity measured; then oxidised in air for 1 h at 623 K and its activity measured at 433 K without any reduction other than that effected by the H_2 at this temperature (temperature programmed reduction showed that this was sufficient to reduce the oxidised Ru). Finally catalysts were again reduced at the original temperature before a last assessment of activity. The changes in rate so produced were quite dramatic (see Table 1).

Table 1. Effect of reduction and oxidation on the activity of Ru/TiO_2 and Ru/SiO_2 catalysts for n-butane hydrogenolysis at 433 K [rates in $10^2 \times$ mol (g Ru)$^{-1}$ h^{-1}].

Treatment	1% Ru/TiO_2	5% Ru/TiO_2	1% Ru/SiO_2
Reduced 623 K, 16 h	3.8	26.2	17.3
↓ Oxidised 623 K, 1 h	25.4	74.4	14.3
↓ Reduced 623 K, 16 h	6.2	19.9	13.1
Reduced 758 K, 16 h	58.4	36.5	—
↓ Oxidised 623 K, 1 h	161	309	—
↓ Reduced 758 K, 16 h	1.8	2.2	—
Reduced 893 K, 16 h	0.6	7.6	—
↓ Oxidised 623 K, 1 h	124	307	—
↓ Reduced 893 K, 16 h	0.2	5.3	—

---

† On leave of absence from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 129 Street, Dalian, China.

Increasing the temperature of the first reduction from 623 to 758 K causes an increase in activity which is most marked with 1% Ru/TiO_2. This is the converse of the usual SMSI effect, but is attributed to the improved removal of Cl^- at the higher temperature. Reduction at 893 K gives lower activities, especially with 1% Ru/TiO_2: this is perhaps a 'normal' SMSI effect, which is apparently achieved at a temperature higher than the usual 773 K in the case of Ru. The oxidations produce activity increases from 3 to 200 fold. Oxidised Ru species are thought to spread over the TiO_2 surface from Ru particles formed in the first reduction, giving after reduction at 433 K highly dispersed Ru^0, perhaps as two-dimensional rafts. This occurs whatever the activity of the metal after the first reduction, but it is inhibited after reduction at 623 K, perhaps because of residual Cl^- on the support. The amount of this well-dispersed Ru^0 is two to three times greater with the 5% Ru/TiO_2.

Activity decreases of 15 to 30 fold occur after the second reduction at 758 K; this is because well-dispersed Ru^0 passes more easily to the SMSI state than the particles formed initially. After the second reduction at 893 K, rates are about the same as after the first reduction: the SMSI condition has been restored.

Significant changes in Arrhenius parameters and product distribution accompany these treatments. Activation energies are lower after oxidation in five of the six cases, and selectivity to methane is usually much increased. This difference permits attribution of the origin of the activity after the second reduction: at 623 K it is due to some dispersed Ru which has not succumbed to SMSI; at 893 K, to some particulate Ru not dispersed during oxidation.

The same treatments applied to 1% Ru/SiO_2 at 623 K (see Table 1) produce no meaningful activity changes, but similar differences in activation energy and in product distribution to those described above are observed.

Received, 7th July 1983; Com. 911

References

1 S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.
2 E. I. Ko and R. L. Garten, *J. Catal.*, 1981, **68**, 233.
3 U.S. Patent 1 576 848 (1976).