Metal–Support Effects in the Catalytic Hydrogenation of CO over Ruthenium Y-Zeolites: Influence of Zeolite Basicity on Olefin Selectivity

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The electronic interaction between small metal crystallites and basic or electron-donor sites in zeolite Y enhances the olefin selectivity of ruthenium in the hydrogenation of carbon monoxide to hydrocarbons.

Limitations on hydrocarbon chain growth have been observed in recent studies on the hydrogenation of carbon monoxide over ruthenium[1] and iron[2] encaged in zeolite Y. These deviations from normal Schulz–Flory behaviour have been attributed[3] to a metal particle size effect whereby the maximum hydrocarbon chain length is restricted by the dimensions of the metal crystallites entrapped in the zeolite structure.

Further control of selectivity towards unsaturated hydrocarbons is related to the adsorption behaviour of the supported metal which may be influenced by interactions with the support. For instance, small metal crystallites encaged in acidic zeolites exhibit an electron deficient character.[4]

The role of basic[5] or electron-donor[6] sites in adsorption and catalysis by alkali metal-exchanged zeolites has not received much attention. The favourable olefin selectivity caused by basic promoters in conventional iron catalysts suggests that metal interactions with basic or electron-donor sites in zeolites may have an important influence on selectivity. We report here some preliminary findings which support this assertion.

A series of Y-zeolites containing either Na^+ or Na^+ and K^+ or Cs^+ as majority charge balancing cations was prepared. Ruthenium was subsequently introduced by partial ion exchange using $Ru(NH_3)_6Cl_3$. Chemical analyses are given in Table 1. Samples of catalyst (200 mg) were outgassed (1.3×10^{-4} Pa) at 673 K for 8 h and reduced in flowing hydrogen at 623 K for 10 h. The synthesis reaction was performed at 1 atm in a flow microreactor at a temperature of 493 K using a $H_2:CO$ ratio of 2; CO conversions were maintained at 1 to 2%. The average ruthenium crystallite size in used samples of the RuNaY catalyst, calculated from hydrogen chemisorption measurements, was 2 nm. Chemisorption measurements on the potassium- and caesium-exchanged samples were not carried out. However, data obtained[7] for a variety of cation modifications of zeolite Y, containing similar ruthenium loadings and prepared in an identical way, indicate that the ruthenium crystallite sizes may be expected to be closely similar irrespective of the observed variation in ruthenium content.

The product selectivities obtained after 15 min on stream are given in Table 1. A marked increase in the olefin selectivity of ruthenium is observed as sodium ions in the zeolite are replaced by potassium or caesium ions. Oxygen anions bound to aluminium cations $[AlO_4]^-$ have been proposed[8] as basic sites in alkali metal-exchanged zeolites. The extent to which the negative charge is shielded by the alkali metal cation decreases as the size of the cation increases and its charge density decreases. The electron-donor strength of the zeolite is therefore expected to increase in the direction NaY < KY <CsY. The electron concentration in the metal would increase accordingly, thus increasing electron donation to carbon monoxide and raising its heat of adsorption, while at the same time suppressing the adsorption of hydrogen and

Table 1. Selectivity[a] of ruthenium zeolite catalysts.

Zeolite unit cell composition[b]	C_1	C_2	C_3	C_4	C_5	C_2 (unsat.)/C_2 (sat.)	C_3 (unsat.)/C_3 (sat.)
$(Ru)_{0\cdot95}(Na)_{52\cdot6}(SiO_2)_{137}(AlO_2)_{55}$	36.8	13.7	25.6	17.3	6.7	0.7	3.7
$(Ru)_{1\cdot2}(Na)_{3\cdot4}(K)_{48\cdot0}(SiO_2)_{137}(AlO_2)_{55}$	42.6	14.8	23.6	13.0	6.0	1.7	5.9
$(Ru)_{1\cdot6}(Na)_{20\cdot0}(Cs)_{29\cdot3}(SiO_2)_{137}(AlO_2)_{55}$	39.6	10.6	22.6	16.9	10.2	2.9	8.0

[a] Selectivity expressed as mole % CO converted into stated product. [b] After reduction of the metal the balance of the counterions is provided by protons.

lowering the hydrogenating activity of the metal. This is reflected in the observed higher olefin selectivity. A similar trend in the catalytic activity of alkali metal-exchanged zeolites in typical base-catalysed reactions has been found.[8]

The hydrocarbon chain length remains essentially unaffected by the nature of the exchange cation. As mentioned earlier, there is no reason to expect important differences in ruthenium crystallite size in the various zeolite samples used in the conversion experiments, which might lead to variations in the product distribution.

The observed shift in the olefin/alkane ratios is in line with that found in RuY samples in which the alkali metal cations were largely replaced by multivalent cations or protons. This results in acidic or electron-acceptor properties in the zeolite and electron deficiency in the metal leading[7] to a markedly reduced olefin selectivity.

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