Zeolite Support Effects on CO–Ru Interactions

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Summary An i.r. study of CO adsorption on a series of zeolite-supported Ru catalysts relates strong metal–support interactions to higher zeolite acidity and lower Fischer–Tropsch/methanation activity.

In recent studies of Fischer–Tropsch/methanation (FT/M) reactions, much attention has been directed toward the type of catalyst support used and its interaction with the metal dispersed on its surface. Adsorption properties and reaction activities can be significantly influenced by strong metal–support interactions (SMSI). This preliminary investigation of CO adsorption on Ru dispersed on a series of zeolite supports suggests a trend in strength of support–metal interaction that correlates well with recent activity data for the same zeolites.[1]

TiO_2-supported Ru and Ni catalysts exhibiting SMSI have been shown[2,3] to possess FT/M activity and selectivity differing greatly from conventional SiO_2- and Al_2O_3-supported catalysts. One hypothesis[4,5] is that the SMSI involve a depletion of metal d-electron density, causing a shift in catalytic properties to the left along a row of the periodic table. The manner in which this shift affects a catalyst's activity for a specific reaction depends upon the activity of the particular metal compared with the activity of its left-hand neighbour for that reaction. This effect is not well documented for Ru, since the catalytic behaviour of Tc has not been studied. It has been pointed out that Mo and Re have lower FT/M activities than Ru.[3] One implication of this is that a shift of the type described above might result in a decrease in Ru activity.

This idea appears to be substantiated by a recent FT/M activity study of Ru ion-exchanged into a series of zeolites and reduced at 300 °C. Methanation activity was found to decrease with increasing support acidity; this implies decreasing activity with increasing electron deficiency of Ru, since increasing zeolite acidity has been related to increasing electron-deficient character of the supported metal.[5]

Other interpretations[6,7] of the fundamental roles of the support and metal in FT/M catalysts can be found in the literature. Some of the ideas put forth concerning Ru on conventional supports conflict with the hypothesis stated above for a Ru catalyst with strong support interaction. Our investigation used i.r. spectroscopy to probe CO adsorption sites in the hope that information about these support–metal interactions would help to resolve some of the contradictions.

Catalysts were prepared by an ion-exchange technique for a nominal metal content of 3% Ru. Zeolites used were, with Si/Al ratio in parentheses, X (1·0—1·5 : 1), Y (1·5—3·0 : 1), L (3·0 : 1), and Zeolon (5·0 : 1). Decomposition of the metal complex left the metal as close as possible to a totally reduced state, as shown by e.s.r., i.r., and volumetric studies[8] with an RuY system. An XPS[9] study with a similar RuY system has also shown that reduction to the metallic state is possible. CO adsorption was carried out overnight at 25 °C, and most of the CO in the gas phase was removed prior to taking i.r. spectra. A Digilab Fourier Transform Infrared spectrophotometer was used. Previous i.r. work[8] had revealed a very complex spectrum for CO adsorption on RuY, and our results show that this is true for other Ru zeolites as well. The Figure shows the CO adsorption regions for the four catalysts in order of increasing acidity of the support.

Our results for CO adsorption show a marked upward shift of the entire linearly adsorbed CO spectral region as catalyst acidity increases. Increasing also with acidity is the relative importance of higher frequency peaks within each spectrum. The broad, very strong band centred around 2000 cm^{-1} in RuX has diminished greatly in RuZeolon, as the whole region shifts above 2000 cm^{-1} and the high frequency side of the region becomes dominant. It appears unlikely that this trend can be explained by any systematic change in Ru structure through the zeolite series. It has been shown[10] for Pd and Pt supported on zeolites that structural changes from the bulk metal are not important.

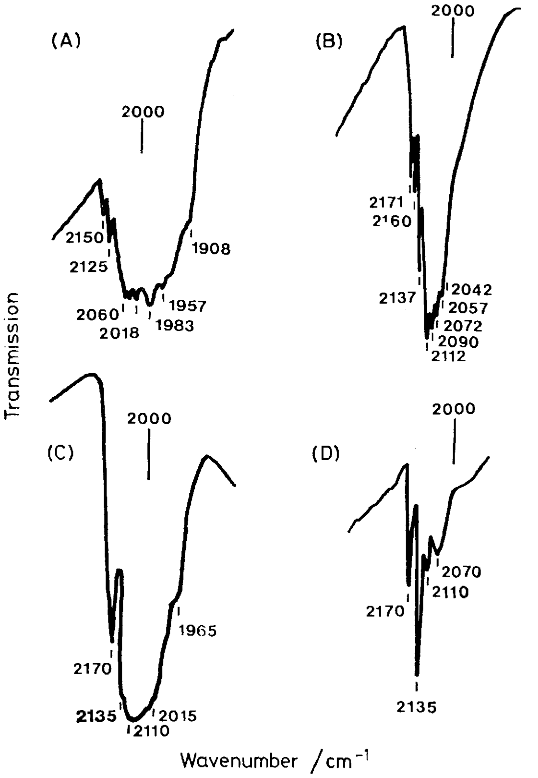

FIGURE. CO adsorption on Ru zeolite catalysts at 25 °C. Si/Al ratio in parentheses. (A) RuNaX (1·0—1·5 : 1), (B) RuNaY (1·5—3·0 : 1), (C) RuKL (3·0 : 1), (D) RuNaZeolon (5·0 : 1).

High frequency peaks due to very stable CO bonding imply strong metal–support interaction as follows: the SMSI leave the metal electron-deficient and capable of only weak bonding to the carbon, hence causing less destabilization of the CO bond. Therefore, as support acidity increases from X to Y to L to Zeolon, a significant increase in SMSI can be seen. This result, correlated with activity data cited previously[1] for these zeolites, offers strong support for the hypothesis that an increase in electron deficiency in Ru would result in lower FT/M activity.

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