Influence of Crystallite Size on Carbon Monoxide Methanation

The effect of crystallite size on carbon monoxide hydrogenation is of great interest to researchers in methanation and Fischer–Tropsch both from its own point of view and its relationship to metal–support interactions (*1*). Recently several workers documented such effects for SiO_2- and Al_2O_3-supported nickel (*2–6*). Activity for methanation increased with crystallite size but showed vaguely defined maxima. Precision of these data suffered because surface areas and crystallite sizes were usually determined on freshly reduced catalysts while activities were measured in separate experiments. Important factors such as degree of reduction and initial crystallite size distributions depend upon handling and reducing procedures (*7*) and cannot be duplicated exactly. Furthermore, van Meerten *et al.* detected crystallite growth induced by nickel carbonyl during the reaction (*3*) so that the nickel surface area continually changed. These features render comparison of areal rates and dispersion difficult. Basing areal rates on measured surface areas of used catalysts is more realistic (*2*), but the extra handling procedures still introduce uncertainties.

We have overcome these difficulties by conducting all experiments in the same cell (*8*). Accordingly, magnetic measurements (for crystallite size) and hydrogen chemisorption (for nickel surface areas) are made at any time during a reaction experiment. Areal rates are precisely obtained with only uncertainties inherent in the techniques themselves and not in sample manipulation or treatment. Measurements were made of CO methanation rates during runs in which the crystallite size grew presumably through interparticle transport via nickel

carbonyl, thus providing an almost continuous record of the size dependence of areal rates. In view of the importance of this subject, we present them in this note, together with other aspects critical to interpretation of these effects.

The sample was 32 wt% Ni/SiO_2 prepared by homogeneous deposition (*7*). Reduction was at 673 K in hydrogen for 4 h. Magnetic measurements and interpretation were made with the same procedures reported earlier (*8*), as were hydrogen chemisorption determinations. Methanation was carried out *in situ* in a flow system. The feed gas contained about 20% CO in hydrogen and was maintained at such a rate to keep the conversion less than 5% and the reactor differential. Temperature of reaction was 500 K. No products other than methane were detected with a standard TC chromatographic apparatus.

Typical crystallite size distributions are shown in Fig. 1. Initially the catalyst was fairly monodispersed with an average volume radius of 1.5 nm. The saturation magnetization corresponded to a degree of nickel reduction of 70.8%. The crystallite size distributions in the first two columns of Fig. 1 were obtained by interrupting the reaction at the indicated times, cleaning the catalyst in flowing helium, cooling and measuring the magnetic properties at 298 and 77 K, followed by hydrogen chemisorption at 298 K. The distributions broadened as reaction proceeded, with both small and large crystallites appearing. After about 12 h, the distribution was very broad with a volume average of 3.8 nm. At this point, the CO concentration was increased to 25%, with an apparent shift to larger crystallites. Purely thermal treatment at 873 and 973 K
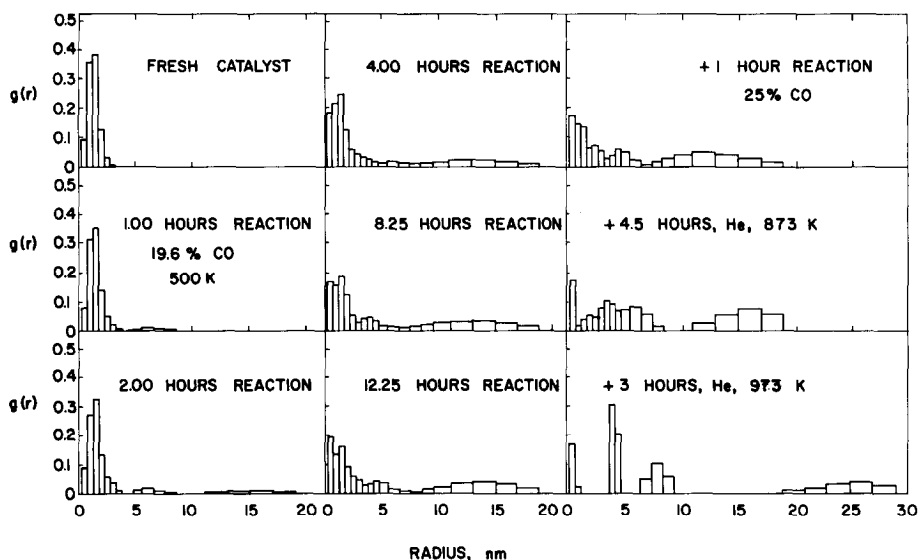
FIG. 1. Crystallite size distribution changes during methanation.

were then carried out, with extensive thermal sintering obvious.

During these sequences of measurements, the saturation magnetization did not change. This is significant since it indicates that (1) the amount of reduced nickel did not increase due to more reduction by the feed, (2) no appreciable surface poisoning by chemically bound carbon was detected, and (3) no metal–support interaction involving electron transfer occurred. Additional reduction would have resulted in an increase of saturation magnetization. Carbon deposition reduces the value and, at these dispersions, is sensitive to surface coverages as low as 5%. Similarly, support interaction leading to electron transfer would be easily detectable. It is possible, but unlikely, that the factors could be all present and compensate each other.

Hydrogen chemisorption measurements were even more revealing. Figure 2 shows the results of several runs similar to Fig. 1. The nickel surface areas measured by extrapolation of the hydrogen chemisorption isotherms to zero pressure have been divided by the area calculated from the appropriate crystallite size distribution and plotted against the magnetic average volume crystallite radius. Surface areas below those calculated from distributions have been attributed to inaccessibility of the surface due to interaction with the support or trapping in pores (9). In thermal treatments, the degree of accessibility was found to decrease as the size increased (10) and was sensitive to the relative size of the crystallite and the pore.

The accessibility factor decreased from 0.5 to 0.2 as the crystallites grew. Although this is a reliable measure of available surface, it is not possible to conclude which parts of the distribution suffer the most loss.
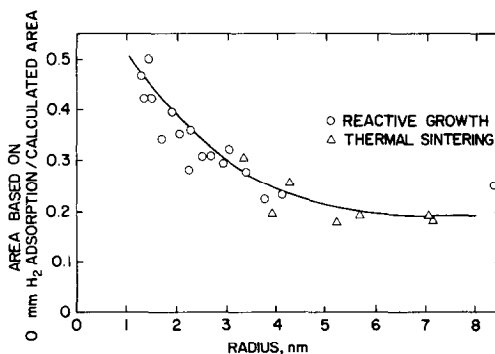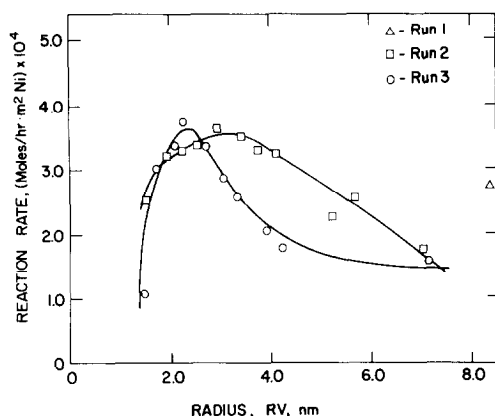

FIG. 2. Degree of accessibility.

FIG. 3. Areal rates versus magnetic volume average.

Using measured surface areas, areal methanation rates are plotted in Fig. 3 against the magnetic volume average from the distributions. Three runs are included for comparison. Rates vary by a factor of about 4, passing through a maximum at 2–3 nm. Differences in the runs reflect variations in crystallite size distributions, emphasizing that average volume does not adequately describe the effect. To adjust for this, Fig. 4 shows rates plotted against dispersion as calculated from magnetic measurements.

Correlation for all runs is much better and the optimum value clearly defined. Comparison of these results with previous data is difficult. The best available are those

of Vannice (2) and Bartholomew et al. (6). Vannice's crystallite sizes were measured by X-ray diffraction line broadening on used catalysts and turnover numbers reported at 548 K for 25% CO in H_2. However, corrections for degree of reduction were not made. Nevertheless, extrapolating two samples to 500 K give turnover numbers of $3–6 \times 10^{-3}$ sec^{-1} for 8% dispersion, compared with 3.04×10^{-3} sec^{-1} from Fig. 4. The data of Bartholomew et al. did account for nickel reducibility but no independent crystallite size measurements were made. Furthermore, turnover numbers at 525 K were for 1% CO. These authors found the same trend as in Fig. 4 and, allowing for differences in dispersion values, reported a maximum value corresponding to 2.1×10^{-3} sec^{-1} compared to 3.81×10^{-3} sec^{-1} for our data. In view of the large variations in experimental conditions, these comparisons are reasonable. The importance of systematic, in situ measurements, such as those reported here, is emphasized.

Vannice interpreted the maximum as a "volcano" curve in which CO is much more strongly adsorbed on smaller crystallites (2), possibly in a precarbonyl form as proposed by Pannel and Bartholomew (11). Ponec, however, has suggested that the smaller crystallites deactivate more through carbon formation (1). No effort
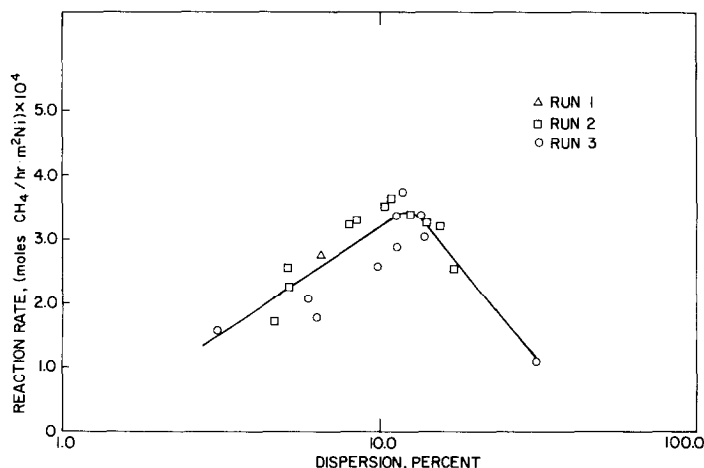

FIG. 4. Areal rates versus magnetic dispersions.

was made to remove any surface carbon by hydrogenation prior to our magnetic measurements. If, as Ponec claims, the surface of small crystallites is deactivated by carbon, then the saturation magnetization of the sample should change. Since this was not the case, we conclude that Vannice's rationale for the optimum is more reasonable and the shape of the curve owes its origin to differences in adsorption and reactivity on different size-dependent sites.

ACKNOWLEDGMENT

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