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DISPERSION OF COPPER SUPPORTED ON SILICA AND METHANOL REFORMING REACTION

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Turnover frequency, activation energy and selectivity of the methanol reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$ varied greatly with the specific surface area of metallic copper, when the title reaction was carried out over copper supported on silica. It was indicated that the reaction was strongly affected by the dispersion of copper.

Methanol is decomposed into hydrogen and carbon monoxide, formaldehyde or methyl formate over metal catalysts (1). However, this species is selectively transformed into carbon dioxide and hydrogen in the presence of water over copper-containing catalysts (2) due to the methanol reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$.

In the present work, the title reaction was carried out over copper supported on silica. The kinetic parameters such as the turnover frequency, activation energy and the selectivity of the reaction were strongly dependent upon the specific surface area of metallic copper. It was indicated that the reaction was sensitive to the dispersion of copper and the mechanism of the reaction was influenced by the catalyst preparation.

The catalyst was prepared either by kneading method or ion exchange. In the former method, copper hydroxide was prepared by addition of copper nitrate solution into sodium hydroxide solution and was then kneaded with silica. In the latter method, copper tetrammine complex solution was prepared from copper nitrate and ammonia, and the complex cation was exchanged with hydroxyl hydrogen on silica surface. Some of experiments were carried out over support-free catalyst which was prepared from copper hydroxide. All catalysts were prepared at pH=11-12, so that anion in the starting material was practically not incorporated in the catalyst (3). The catalysts thus prepared were dried at 120° C overnight and calcined in air at 500° C for 3 hrs.

From XPS and AES analyses, it was confirmed that no nitrate anion, sodium cation or ammonia or these fragments remained on the surface.

The experiments were carried out in a flow system. The equimolar mixture of water and methanol was fed in a nitrogen stream with micropump and was vaporized in the preheater before entering in the catalyst bed. The products and the reactants were analyzed by gas chromatography.

The surface area of metallic copper was determined by the nitrous oxide adsorption according to the method proposed by Scholten et al. (4). Silica employed as a support was commercially available (Japan Chromato-Industry Co.).

When the methanol-water mixture was admitted over copper containing catalysts, the reaction occurred slowly around 150°C. As the catalyst was gradually reduced, the rate of the reaction increased and the steady state was attained. Once the catalyst was reduced, the activity of the catalyst was stable under given conditions.

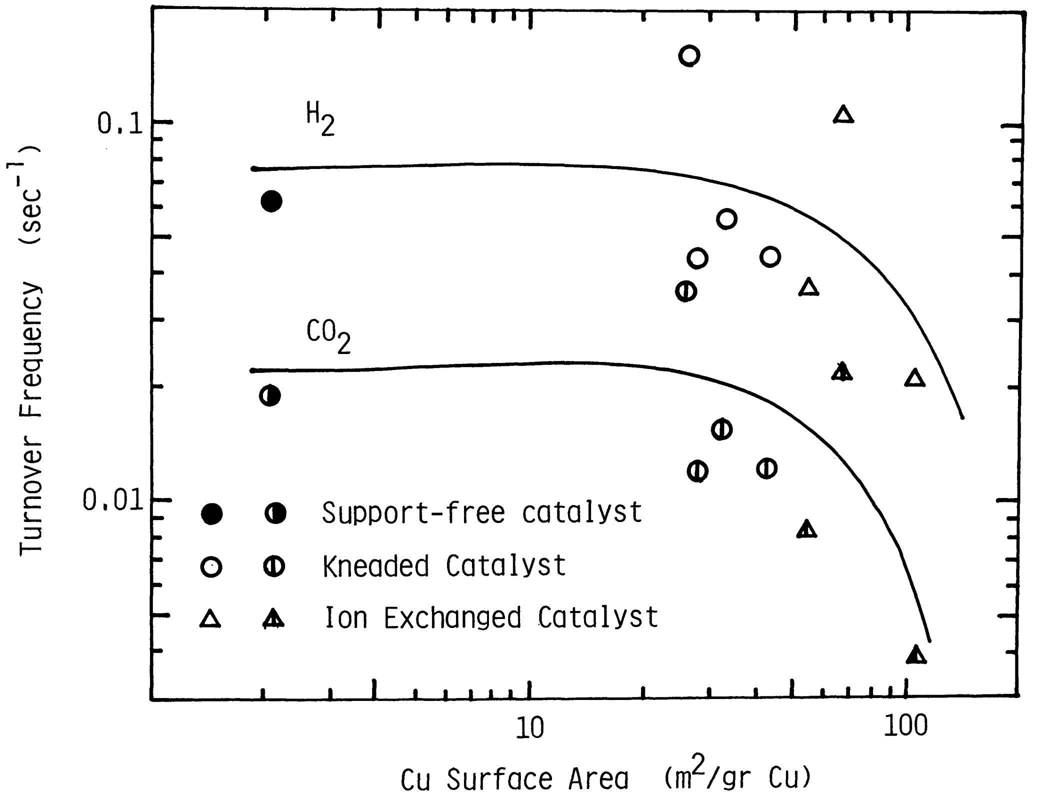

Figure 1 Turnover Frequency and the Specific Surface area of Copper

In Figure 1, the turnover frequencies obtained at 220°C are plotted against the specific surface area of metallic copper (the surface area of metallic copper alloted for the weight of copper used). The results are somewhat scattered but it evidently shows the turnover frequency decreases with the increase in the surface area when it exceeds 50 m^2/gr Cu used (hereafter referred to as region I). However, when it was smaller than 50 m^2/gr Cu (hereafter referred to as region II), the turnover frequencies

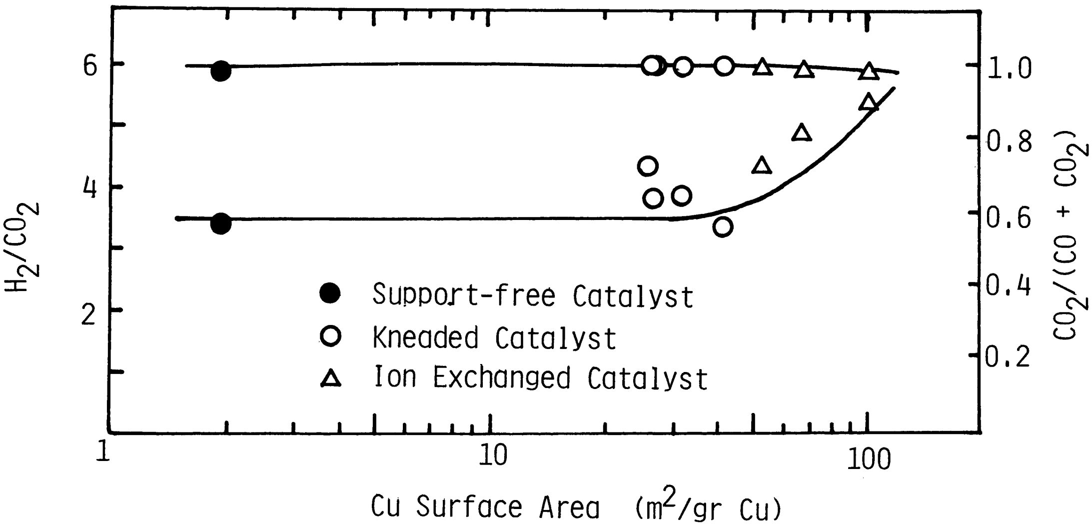

Figure 2 H_2/CO_2 and $CO_2/(CO + CO_2)$ vs. specific surface are of copper

obtained were practically the same as that obtained on support-free copper catalyst and remained constant irrespective of the specific surface area. In Figure 2, the parameters H_2/CO_2 and $CO_2/(CO + CO_2)$ at the outlet of the catalyst bed are plotted against the specific surface area of metallic copper. It shows that the former is kept around three while the latter being unity in region II. The reforming reaction proceeded selectively. In region I, on the other hand, the parameter H_2/CO_2 was increased with increase in the specific surface area while the parameter $CO_2/(CO + CO_2)$ was practically kept at unity over the whole range of the surface area. Figure 3 shows the plots of the activation energy versus the specific surface area of metallic copper. In accordance with the above results, the activation energies obtained were also markedly varied in region I as the specific surface area was increased.

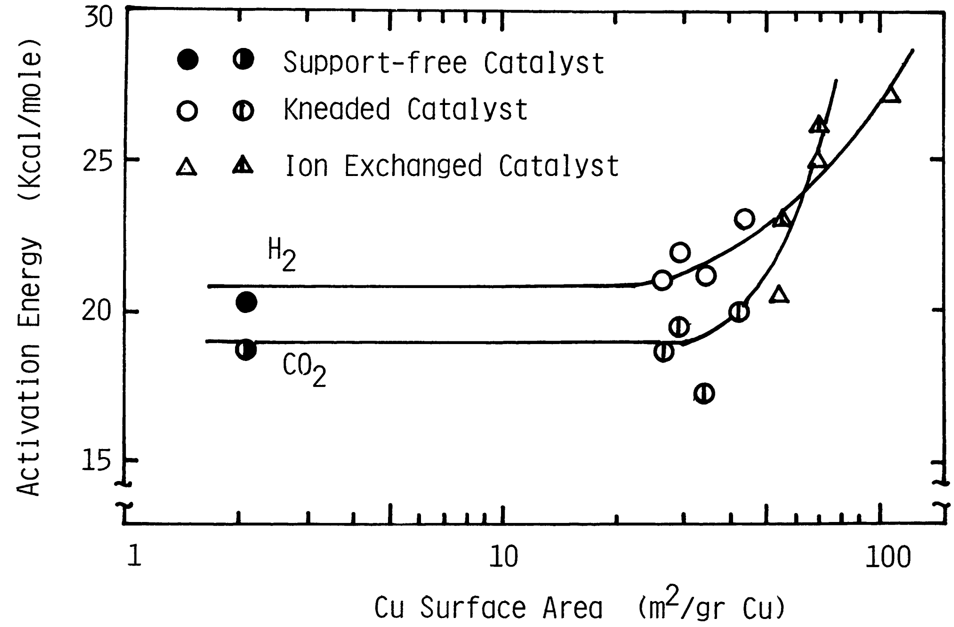

Figure 3 Activation Energy vs. Specific Surface area of Copper

On the other hand, these values remained constant in region II. The present results, therefore, evidently demonstrated that the kinetic parameters related to the methanol reforming reaction depended upon the surface area of metallic copper. The reaction was highly sensitive to the dispersion of copper and the mechanism of the reaction would vary when the specific surface area being 50 m^2/gr Cu used.

The metallic copper particle size was estimated to be below 12 nm when the specific surface area was over 50 m^2/gr Cu used. This was, however, somewhat larger compared with the size for which so-called crystal size effect was observed (5,6). In a preliminary experiment, it was found that the catalyst in region I was reduced only partly with hydrogen, while the catalyst in region II was completely reduced (7). The metallic copper surface area alloted for the weight of metallic copper actually present should be different from that alloted for the weight of copper used. The particle size of metallic copper cluster would be, therefore, different from that estimated from the latter value in particular for the catalyst in region I.

The details of the effect of the dispersion found in the present work are currently under investigation (8).

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8) One of referees reviewed that Cu(I) might be the active site for the reaction particularly in region I where the catalyst was incompletely reduced with hydrogen. This should be also examined in the future study.

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