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NOTES

Effect of Aluminium Oxide on the Properties of Cu–Mo Catalyst in the Oxidative Dehydrogenation of Butene-1 to Butadiene

Copper molybdate catalysts show catalytic activity for the oxidative dehydrogenation of butene-1, giving butadiene and carbon dioxide as main products, but not for its isomerisation to butene-2 (*1*). The isomerisation reaction is catalysed at the centres of acidic nature; thus, aluminium oxide and aluminium molybdate catalysts having such acidic properties may be active catalysts for the conversion of butene-1 to butene-2. The effect of composition on the activity of a Co–Mo system, the influence of surplus trioxide of molybdenum on properties and catalytic activity of a Cr–Mo catalyst, and the effect of molybdenum trioxide on physicochemical and catalytic properties of some molybdates have been studied earlier (*3, 4, 5*). Here, the effect of supplementary aluminium oxide giving rise to extra acidic centres in copper molybdate catalyst has been studied with regard to the activity of the catalyst in the reaction of oxidative dehydrogenation of butene-1 to butadiene in the temperature range of 285 to 450°C in a continuous fixed-bed reactor. Introduction of extra acidic centres in copper molybdate catalyst by supplementary aluminium oxide provides a way to establish how much the acidity of the catalyst surface serves to affect the oxidative dehydrogenation of butene-1 to butadiene.

Cu–Mo oxide catalysts with supplementary aluminium oxide were prepared by two methods: (1) coprecipitation, and (2) shower impregnation. According to method 1, samples were prepared by mixing aqueous solutions of ammonium paramolybdate, copper nitrate and aluminium nitrate at room temperature. After drying at 120°C, the samples were fired at 500°C for a period of 10 h in a furnace. In the second method the catalyst was prepared by showering an aqueous solution containing a known quantity of aluminium nitrate onto a copper molybdate catalyst. The sample was dried at 120°C and fired at 500°C for a period of 5 h. X-ray investigations were carried out on a DRON-I-type X-ray spectrometer using Cu$K\alpha$ rays. Infrared spectra were taken in the frequency range 400–1000 cm^{-1} on an UR-20 IR spectrometer.

The activity of the catalyst for the oxidative dehydrogenation of butene-1 was studied in the temperature range 285 to 450°C using a continuous reactor. Other operating conditions were: ratio butene-1 : air, 1 : 11; space velocity, 1500 h^{-1}; volume of catalyst, 5 cm^3; and particle size of the catalyst, 1–2 mm.

X-ray analysis of the synthesised catalyst showed that phases of free aluminium oxide were absent. In the diffraction patterns of catalyst samples with different compositions of aluminium oxide prepared by both methods, no shifts in the diffraction maxima were revealed; however, redistributions of the relative intensities of characteristic diffraction peaks were observed [Figs. 1(a) and 1(b)].

The changes in distribution of intensity of diffraction maxima upon introduction of aluminium oxide in copper molybdate may indicate some distortion of the molybdate structure. The sharpest change in peak intensity takes place in the range 0.05 to 1 wt% aluminium oxide content and depends on the method of preparation of catalyst samples. In the case of coprecipitated samples, the diffraction peaks pass through maxima at a composition of 1 wt% and in

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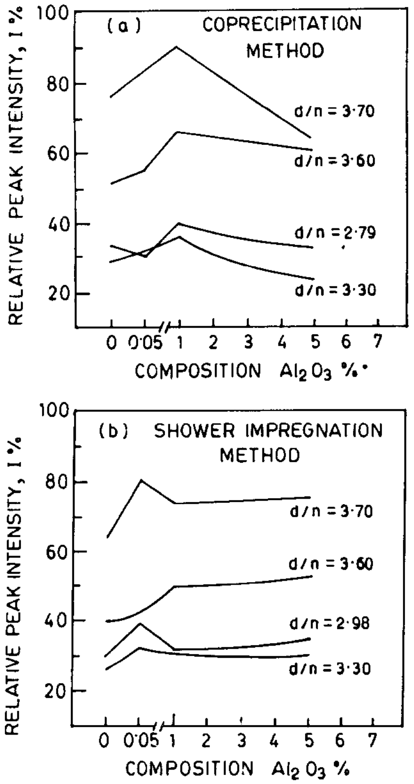

FIG. 1. The effect of aluminium oxide composition (wt%) on relative peak intensities of some characteristic X-ray diffraction peaks (X-ray study plots).

the case of impregnated samples at 0.05% by weight of aluminium oxide.

Introduction of oxides of aluminium up to 5 wt% does not lead to any shift in the characteristic absorption bands in the IR spectra of copper molybdate. However, it changes the relative optical density in the region near this absorption band, which could be attributed to a change in some characteristic metal–oxygen bonds.

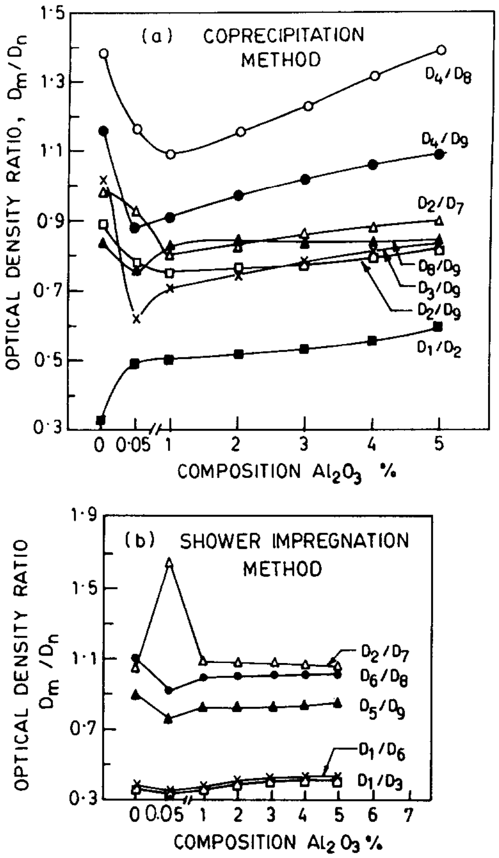

FIG. 2. Change in relative optical density D_m/D_n versus composition of catalyst Al_2O_3 (wt%) (IR spectroscopy study plots). D_m and D_n are optical densities such that $D_m = \log I_o - \log I_m$ and $D_n = \log I_o - \log I_n$, where I_o is the intensity of reference peak, i.e., of maximum height, and I_m and I_n are heights of mth and nth peaks. Values m and n are positive integers, 1, 2, 3, 4, ... , etc.

From Figs. 2(a) and 2(b), it is evident that the sharpest change in optical density of samples prepared by coprecipitation occurs in the range 0.05–1 wt% and in the case of shower impregnation after addition of 0.05 wt% aluminium oxide. Thus data from both IR spectroscopy and X-ray diffraction indicate that, depending on the method of preparation of the catalyst, a distinct change in the structure of the catalysts occurs in the range 0.05–1 wt% of aluminium oxide.

Determination of the activity of the catalyst showed that by increasing the amount of oxide of aluminium in the copper molybdate catalyst, the conversion of butene-1 was increased. Under these conditions an enhanced rate of formation of carbon dioxide was observed. The specific rate of formation of butadiene and products of isomerisation in the temperature range 300–390°C proceeded through maxima on addition of 1 wt% Al_2O_3; total oxidation, i.e.,

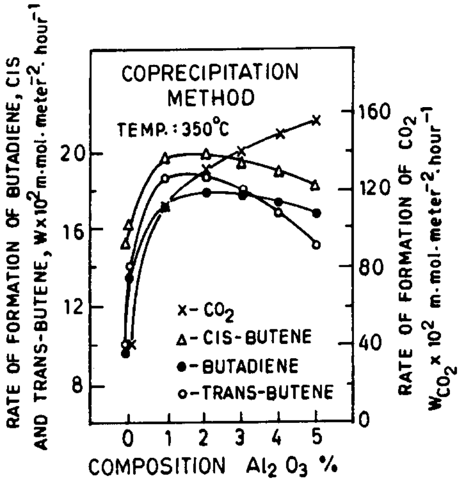

FIG. 3. Rate of formation of products of oxidative dehydrogenation of butene-1 versus composition of catalyst Al_2O_3 (wt%).

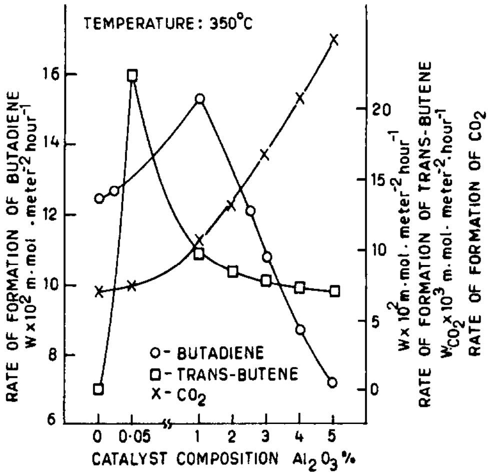

FIG. 4. Shower impregnation method. (○) Butadiene, (□) *trans*-butene, (×) CO_2. Rate of formation of products of oxidative dehydrogenation of butene-1 versus composition of catalyst Al_2O_3 (wt%).

combustion, occurs at still higher temperatures.

Figures 3 and 4 show the change in specific rate of formation of products of butene-1 at 350°C versus quantity of promoter, i.e., the percentage of aluminium oxide introduced into the Cu–Mo catalyst system, prepared by the coprecipitation method and the shower impregnation method, respectively. The rate of formation of carbon dioxide grows without any break with an increase in the content of Al_2O_3, and the specific rates of formation of butadiene and isomers of butene-1 pass through maxima at 1 wt% aluminium oxide in the case of coprecipitated catalyst. Thus, rate of formation of butadiene and products of isomerisation change in a similar manner. But in the case of shower-impregnated catalysts, the rate of formation of butene-2 passes through a maximum at 0.05 wt% aluminium oxide, which can be attributed to the change in the structure of the catalyst at this composition as evidenced by X-ray and IR study plots (Figs. 1(b) and 2(b), respectively). Also, it leads to the conclusion that a larger number of active acidic centres are available at the surface of the shower-impregnated catalyst even at 0.05 wt% aluminium oxide composition. However, the rate of formation of butadiene also passes through a maximum at 1 wt% aluminium oxide in the shower-impregnated catalyst.

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