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A NOVEL METHOD FOR MEASURING BASE STRENGTH DISTRIBUTION ON BASIC SOLID CATALYSTS UNDER OPERATING CONDITIONS

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Stepwise thermal desorption (STD) of CO_2 with gravimetric analysis of the desorbed CO_2 from 50–900 ° C provides a simple and faster method for measuring total basicity and base strength distribution on basic solid catalysts under their operating conditions.

Acidity of solid catalysts [1–3] has been investigated very widely but very little work on their basicity has been carried out so far [3,4]. Importance of basic solid catalysts in many industrially important reactions has been emphasized recently by Tanabe [4]. Oxidative coupling of methane to C_2-hydrocarbons, which is of a great practical importance, is also catalysed by basic solid catalysts. For better understanding of base catalysed reactions, it is essential to know the base strength distribution on basic solid catalysts, particularly, measured at their operating temperatures. In the present communication, a novel but simple method based on stepwise thermal desorption of carbon dioxide for the above purpose has been described and illustrated by carrying out measurements on MgO and CaO calcined at two different temperatures.

MgO and CaO catalysts were prepared by treating MgO (GR, Loba) and CaO (GR, Loba) with deionized water at 90 ° C for 4 h, drying the resulting hydrolysed mass in air oven at 120 ° C for 12 h, pressing and crushing the dried mass to 22–30 mesh size particles and calcining them in muffle furnace under static air at 600 and 950 ° C for 10 h. The surface area of the MgO calcined at 600 and 950 ° C was 70.5 and 11.3 $m^2 \cdot g^{-1}$, respectively and that of the CaO calcined at 600 and 950 ° C was 14.6 and 1.2 $m^2 \cdot g^{-1}$, respectively.

The catalyst (about 1.0 g) was packed in a quartz reactor (i.d.: 9 mm) between quartz wool plugs and pretreated in situ by heating at its calcination temperature in a flow of dry N_2 (20 $cm^3 \cdot min^{-1}$) for 1 h to remove adsorbed water and other adsorbates. Its basic sites were then saturated by chemisorbed CO_2 at 50 ° C in a flow of pure CO_2 (20 $cm^3 \cdot min^{-1}$) for 30 min and the physically adsorbed CO_2 is desorbed in the flow of N_2 (20 $cm^3 \cdot min^{-1}$) for 30 min. The stepwise thermal desorption (STD) of CO_2 was carried out by desorbing the CO_2 chemisorbed at 50 ° C on the catalyst in the flow of N_2 (20 $cm^3 \cdot min^{-1}$) by heating it from 50 to 900 ° C in a number of successive temperature steps (50–150 ° C, 150–300 ° C, 300–450 ° C, 450–600 ° C, 600–900 ° C). The temperature in each step was raised at a heating rate of about 30 ° C $\cdot$ min^{-1}. After the maximum temperature of the respective step was attained, it was maintained for a period of 30 min to desorb the CO_2 reversibly adsorbed on the catalyst at that temperature. The amount of CO_2 desorbed in each step was determined gravimetrically by absorbing it completely in an aqueous barium hydroxide solution and weighing the resulting barium carbonate. When the catalyst was further heated above 900 ° C, no significance desorption of CO_2 was observed. The chemisorption of CO_2 on the catalyst at a temperature, T, was obtained from the amount of CO_2 desorbed from the temperature, T to 900 ° C. In this study, chemisorption is considered as the amount of CO_2 retained by the presaturated catalyst after it was swept with pure nitrogen for a period of 30 min and it is assumed that one site is involved in the chemisorption/desorption of one CO_2 molecule.

The base strength distribution obtained from the STD of CO_2 on the MgO and CaO is shown in fig. 1. The columns show the energy distribution of the sites involved in the chemisorption of CO_2 at the lowest temperature of the STD (i.e. 50 ° C). Each column represents the number of sites measured in terms of CO_2 desorbed in the corresponding temperature step. The strength of these sites is expressed in terms of the desorption temperature of CO_2, T_d, which lies in the range in which chemisorbed CO_2 is desorbed. The sites of strength $T_1 < T_d \leqslant T_2$ could be obtained from the amount of CO_2 which was initially chemisorbed at T_1 and subsequently desorbed when the temperature was increased from T_1 to T_2.

Figure 2 shows the temperature dependence of the chemisorption of CO_2 on the MgO and CaO catalysts. The chemisorption of CO_2 at higher temperature points to an involvement of the stronger sites. The CO_2 chemisorption vs. temperature curves, therefore, present the type of site energy distribution in which the number of sites are expressed in terms of the amount of CO_2 chemisorbed as a function of chemisorption temperature.

Comparison of the results (figs. 1 and 2) reveals the followings. The stronger basic sites per unit weight or per unit surface (measured by the chemisorption of CO_2 at higher temperatures) on the CaO are much larger than that on the MgO. The increase in the calcination temperature from 600 to 950 ° C results in a large decrease in both the total basic sites (measured by the chemisorption of CO_2 to 50 ° C) and the stronger basic sites, per unit weight, on the MgO and CaO, and also causes decrease in the stronger basic sites per unit surface on both the catalysts.

Earlier studies [5] showed that the catalytic activity of CaO (calcined at 950 ° C) in oxidative coupling of methane is much higher than that of MgO

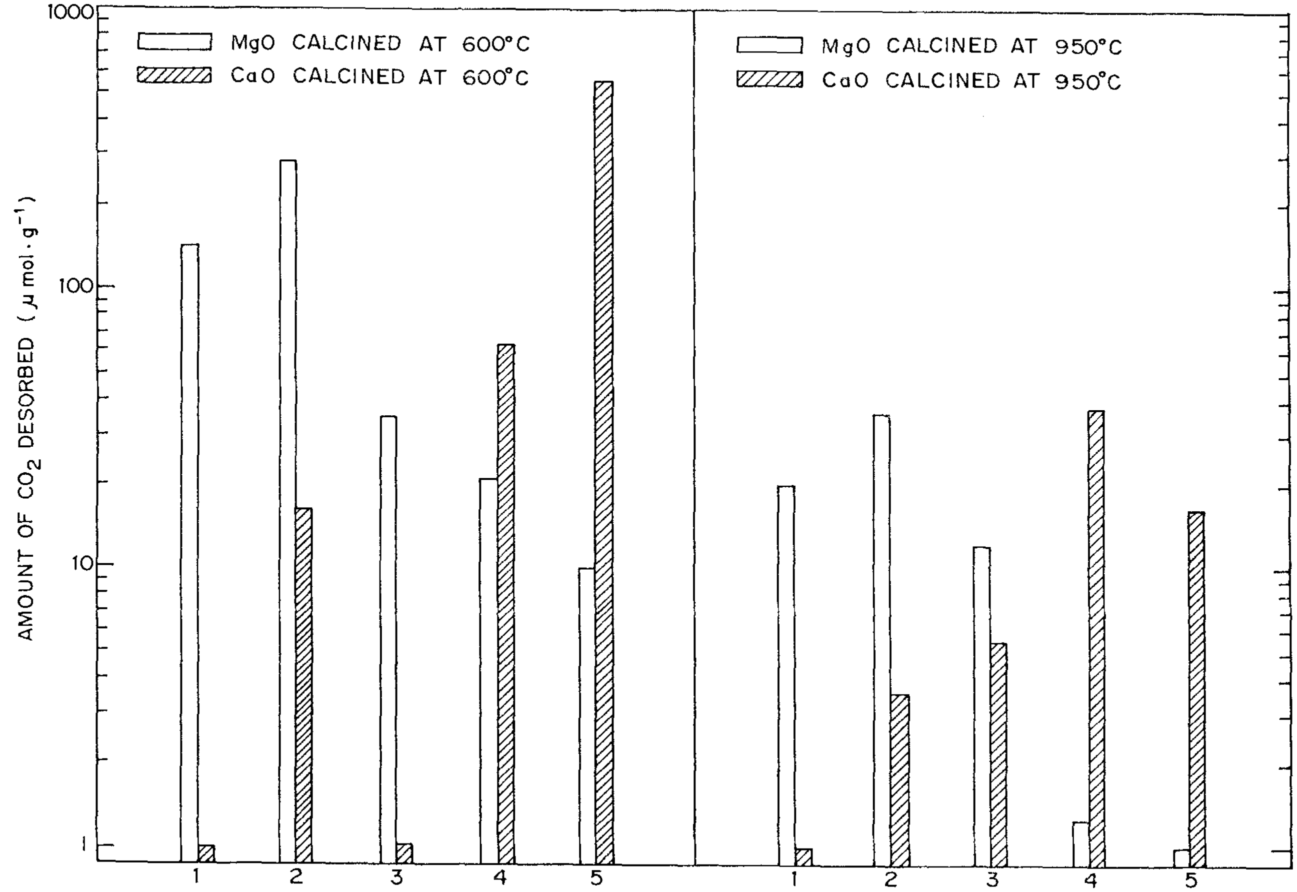

Fig. 1. Base strength distribution on MgO and CaO (calcined at 600° and 950° C) obtained by STD of CO_2 from 50° to 900° C [CO_2 desorption temperature steps: (1) 50°–150° C, (2) 150°–300° C, (3) 300°–450° C, (4) 450°–600° C, (5) 600°–900° C]

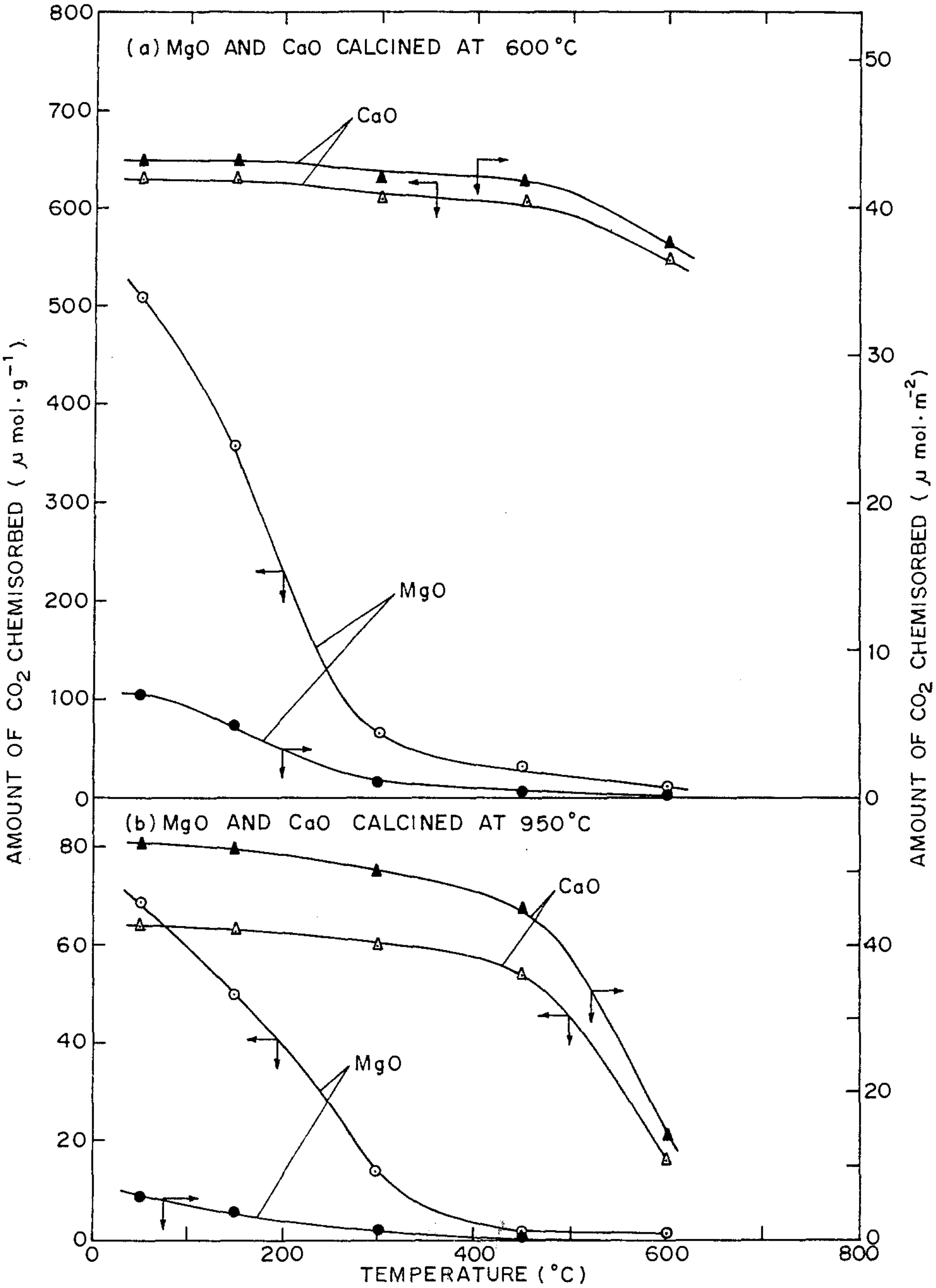

Fig. 2. Chemisorption of CO_2 on MgO and CaO calcined at 600 ° and 950 ° C.

(calcined at 950 ° C). The higher activity of CaO is consistent with its higher strong basic sites (fig. 2b).

The results in table 1 reveal that the doping of MgO with cerium results in a

Table 1
Chemisorption of CO_2 on different solids

Solid	Calcination temperature (°C)	Amount of CO_2 chemisorbed (μ mol·g^{-1})		
		50°C	300°C	600°C
MgO	950	69.4	13.7	1.0
Ce-MgO (Ce/Mg = 0.005)	950	286.6	111.7	75.0
Alumina	900	3.9	2.1	0.2
H-ZSM-8	600	9.1	7.0	4.5

very large increase in the basicity, particularly in the number of strong basic sites. The increase in the strong basic sites is very much consistent with the dramatic increase in the catalytic activity in the oxidative coupling of methane to C_2-hydrocarbons due to the doping; the conversion of methane is increased from 0.6 to 20.3% [6,7]. The chemisorption of CO_2 (at 50–600°C) on a neutral solid (alumina) has been found to be negligibly small. A small chemisorption of CO_2 on the highly acidic H-ZSM-8 zeolite [8] is expected to be due to the presence of small amount of Na^+ cations in the zeolite (Na^+-exchange in the zeolite = 4.0%).

The benzoic acid titration methods for measuring total basicity [9] and base strength distribution [10,11] suffer from the following limitations: These methods are based on use of indicators and the hydrolysis of highly basic solids due to presence of traces of moisture makes the determination of exact end-point of titration very difficult. Also, the basicity measurements are carried out in presence of a solvent at room temperature (i.e. at conditions taken far away from the operating conditions of the catalyst). All these limitations are overcome in the STD method, which provides reproducible data (within about 5%) on both the chemisorption of CO_2 at different temperatures and the distribution of basic sites of different strengths. It may be noted that the methods based on STD of pyridine [8,12–14] and ammonia [15] have been extensively used for measuring acid strength distribution on solid catalysts. When compared to the temperature programmed desorption (TPD) methods, the STD methods have advantages, such as the acidity/basicity distribution data obtained are quantitative and also not influenced by the heat and mass transfer effects.

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