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NOTE

Estimate of the Basicity of Ln_2O_3–Bi_2O_3 Catalysts for Oxidative Coupling of Methane through Diffuse Reflectance UV–vis Experiments

The catalyst basicity has been shown to correlate with the activity and selectivity to C_2 in the oxidative coupling of methane (OCM); in a recent paper, Maitra reviews the effect of basicity on the performances of OCM catalysts (1). However, in the oxides of the rare earth elements series the activity to C_2 in the oxidative coupling of methane does not follow any simple basicity trend (2). The measurement of the basicity of pure oxides is not an easy task and problems can appear due to the existence of structural polymorphism. The decomposition temperature of salts is among the proposed methods for measuring solid state basicity of oxides (1). As earlier reported by our group (3) the decomposition temperature of the lanthanide hydroxides suggests that Lu_2O_3 is as basic as Sm_2O_3. This effect is due to the singular character of $Lu(OH)_3$, which is the only hydroxide in the series with cubic structure. The thermochemical parameters of the decomposition reaction are then affected (3). For the case of supported or mixed oxides the problem of stating the basicity is even more complex. Thus, simple criteria such as the size and charge of a cation may not hold for the basicity sequence. For instance, on increasing the calcination temperature of Sm_2O_3/Al_2O_3 catalysts the crystalline structure of the active phase is modified, which results in altering the basicity of the catalysts as deduced by the change in the activity and selectivity in the OCM (4). Similarly, two Sm/Bi_2O_3 catalysts prepared by different methods show differences in the OCM depending on the crystalline structure. So, a mixture of α-Bi_2O_3 and SmBiOCl-type phases results in higher activities and selectivities than a mixture of tetragonal and fcc-type phases (5).

The present work is aimed toward estimating the basicity of the catalyst based in the electronic structure of the solid. The stabilization of the β-Bi_2O_3 phase due to the presence of rare earth cations (6) allows us to separate the role of the basicity of the catalysts from the influence of the crystalline structure in the activity in the OCM.

Lanthanide-doped (4% M in Sm, Er, and Lu) bismuth oxides were prepared by calcining in air physical mixtures of adequate amounts of both oxides. The mixtures were calcined in air at 1073 K for 18 h. For comparative purposes a similar treatment was performed on pure Bi_2O_3. The specific surface area (S_{BET}) was ca. 0.3 m^2/g for all the catalysts. After the preparation of the catalysts the characterization was carried out by XRD using $CuK\alpha$ radiation and pyrolitic graphite as monochromator. Diffuse reflectance UV–vis spectroscopy was carried out in a Shimadzu spectrometer at room temperature, and when necessary the catalysts were diluted in $BaSO_4$ for preventing signal saturation. Catalytic activity tests were carried out at temperatures ranging from 988 to 1088 K in a fixed-bed flow reactor at atmospheric pressure. The experimental device and catalyst pretreatment have been described in detail elsewhere (4).

The X-ray diffraction pattern of Bi_2O_3 calcined at 1073 K corresponds to the α-phase (Fig. 1). The patterns obtained for the lanthanide modified catalysts match very well that corresponding to the β-Bi_2O_3 phase (6). This tetragonal phase has also been suggested from XRD data for 10% M Yb_2O_3–Bi_2O_3 solid solutions (7). The experimental X-ray data were fitted by using an indexing and least-squares powder diffraction program. Figure 1 shows, as an insert, the obtained unit-cell parameters for the tetragonal β-Bi_2O_3 phases.

The diffuse reflectance UV–vis spectra of the studied catalysts are shown in Fig. 2. The UV–vis spectrum of α-Bi_2O_3 is characterized by a broad band centered at 380 nm. A charge transfer process from the O(2*p*) band to the empty levels of bismuth oxide is responsible for this band. On modifying the crystal structure of bismuth oxide neither the shape nor the position of the UV–vis band is modified. The presence of lanthanide cations in the solid solution resulted in a broader absorption. The absorption maximum peaks at around 465 nm, shifting to higher wavelengths from Sm to Lu. The modification in the UV–vis spectrum due to the presence of the lanthanide cations in the solid solution is better observed by subtracting the spectrum corresponding to pure Bi_2O_3. In this

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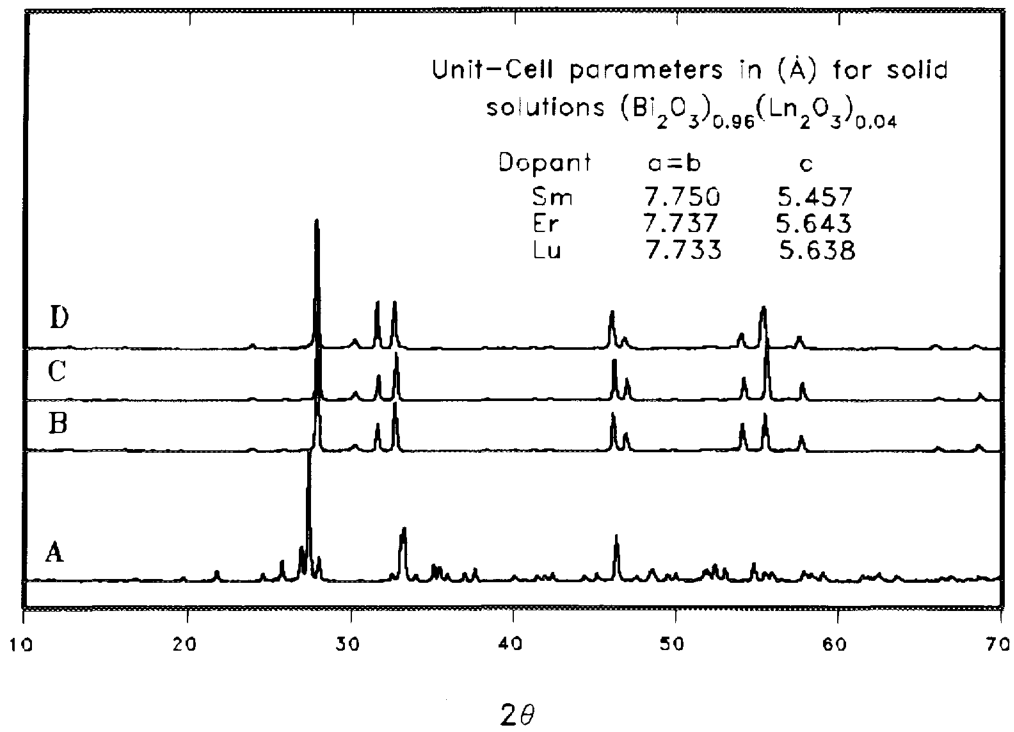

FIG. 1. X-ray powder patterns of Ln_2O_3–Bi_2O_3 solid solution catalysts: (A) α-Bi_2O_3, (B) Lu_2O_3–Bi_2O_3, (C) Er_2O_3–Bi_2O_3, and (D) Sm_2O_3–Bi_2O_3. The calculated unit-cell parameters for the solid solutions are shown in the upper right corner.

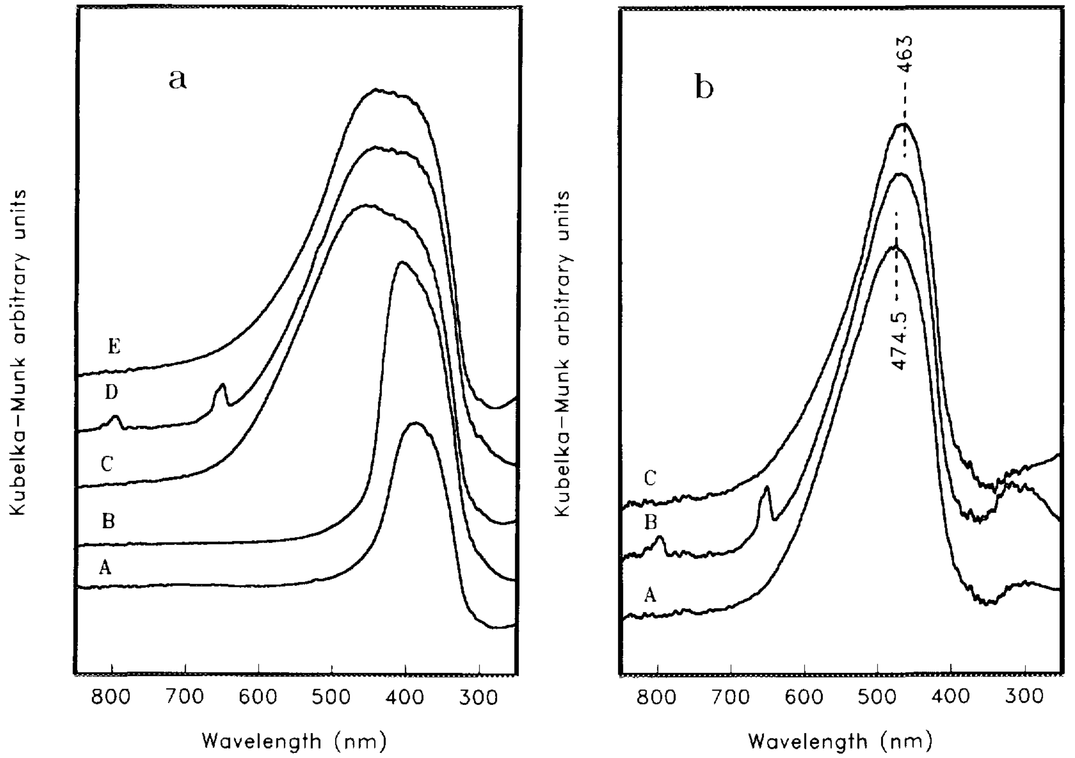

FIG. 2. (a) UV–vis reflectance spectra of the bulk solid solution catalysts: (A) δ-Bi_2O_3, (B) α-Bi_2O_3, (C) Lu_2O_3–Bi_2O_3, (D) Er_2O_3–Bi_2O_3, and (E) Sm_2O_3–Bi_2O_3; (b) UV–vis reflectance spectra resulting after substraction of the α-Bi_2O_3 spectra to that corresponding to the solid solutions: (A) Lu_2O_3–Bi_2O_3, (B) Er_2O_3–Bi_2O_3, and (C) Sm_2O_3–Bi_2O_3.

TABLE 1

Energy (eV) of the O(2*p*) → Bi Transition for Ln_2O_3–Bi_2O_3 Solid Solutions

Catalyst	E_1	E_2
Bi_2O_3	3.05	—
Sm_2O_3–Bi_2O_3	3.05	2.68
Er_2O_3–Bi_2O_3	3.05	2.65
Lu_2O_3–Bi_2O_3	3.05	2.61

way, the absorption is separated into two components. The second component is associated to the presence of rare earth elements (Fig. 2b). The position of the maximum of the band depends on the nature of the lanthanide cation shifting from 474.5 nm for lutetium to 463 nm for samarium. In Table 1 the energy associated to the O(2*p*) → Bi transition as a function of the lanthanide cation is shown. The E_1 value corresponds to the band gap in pure Bi_2O_3 and E_2 corresponds to the same magnitude in the solid solutions.

The main reaction products in the OCM were CO_2, C_2H_4, and C_2H_6. For the highest reaction temperatures and when the $CH_4:O_2$ ratio is low, CO and traces of C_3 and C_4 are observed. Data on the catalytic properties of the solid solutions are given in Table 2. Pure rare earth oxides catalyze the oxidative coupling of methane with higher yields (1), while the activity and selectivity of pure Bi_2O_3 is lower than for the solid solutions. The catalytic activity of our systems compares with the ones reported for a 5 at% Sm/Bi_2O_3 catalyst. This material shows, according to Voskresenskaya *et al.* (5), a mixture of the tetragonal and cubic phases of Bi_2O_3.

The C_2 yield increases on raising the reaction temperature and/or lowering the $CH_4:O_2$ ratio. The same behavior has been observed in many other catalysts used in this reaction (8) and for bismuth-based catalysts (9).

The crystalline structure of the solid (7) and the surface basicity (8) are factors that influence the activity and selectivity of catalysts in the OCM. The Ln_2O_3–Bi_2O_3 prepared show the same crystalline structure. Although the pure Bi_2O_3 presents at RT a monoclinic structure, on increasing the temperature this phase transforms to the tetragonal *β*-phase just below the lowest reaction temperature (9). So, the crystalline structure of all the catalysts studied is the same at the actual reaction conditions. Thus, the observed differences in the activity (Table 2) cannot be associated to differences in the coordination polyhedra of the active site.

TABLE 2

Percentage of Methane Conversion, Selectivity, and C_2 Yield on Bismuth-Containing Oxide Catalysts (0.5 g of catalyst, 60 ml min^{-1}, T = 1088 K, $CH_4:O_2$ = 2.6)

Catalyst	Conv. (%)	Selectivity (%)				C_2 yield (%)
		CO_2	CO	C_2H_6	C_2H_4	
Bi_2O_3	14.36	10.73	53.68	11.67	19.44	4.46
Sm_2O_3–Bi_2O_3	18.93	17.86	46.32	9.48	22.56	6.06
Er_2O_3–Bi_2O_3	19.4	21.23	41.61	7.85	23.75	6.13
Lu_2O_3–Bi_2O_3	20.16	23.55	40.43	7.42	24.88	6.51

The charge transfer process associated to the absorption band in Fig. 2b has to be related to the modification of the O(2*p*) band. This is due to the presence of lanthanide cations in the solid solution. A similar fact has been reported for $KBiO_3$ and $BaBiO_3$ by Papaconstantopoulos *et al.* (10). In these solids they found that the O(2*p*)-dominated band widens by 0.4 eV due to disorder induced by alloying on the Ba and Bi sites. The raising of the top of the O(2*p*) band is similar to that observed in our case (Table 1). According to the electronic structure reported for bismuth compounds having tetragonal structure (11), the charge transfer process may be associated to transitions from the O(2*p*) band to the Bi(6*p*)-dominated one. By plotting the activity to C_2 against the energy of the O(2*p*) → Bi(6*p*) transition (Fig. 3), it can be observed that on decreasing the E_2 value, that is, on raising the top of the O(2*p*) band the activity to C_2 increases.

The general trend observed for the oxides of the group II of the periodic table in the OCM reaction is that the activity increases on increasing the basicity (12). So, for the Ln_2O_3–Bi_2O_3 solid solutions the basicity should increase on decreasing the E_2 value. Then it can be assumed

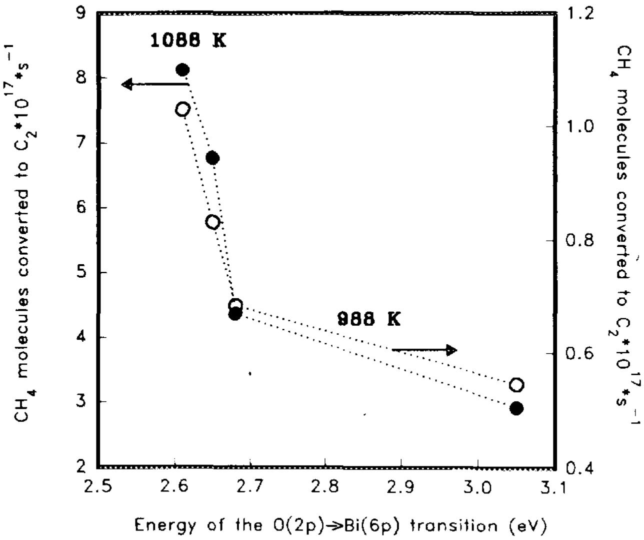

FIG. 3. Variation of the activity to C_2 with the catalyst basicity, measured through the energy of the O(2*p*) → Bi(6*p*) transition.

that the position of the top of the O($2p$) band represents the donating power of electrons of the solid.

It is worth noting that using simple criteria as the charge and size of cations, or the decomposition temperature of salts of pure oxides, the sequence obtained will point to the higher basicity of the solid solution containing samarium. On the other hand, the UV–vis experiments establish that the more basic catalyst is the Lu_2O_3–Bi_2O_3 solid solution. This is also supported by the sequence of activities to C_2. SCF–MO ab initio calculations on small clusters of the type $M(OH)_3$ (M = Al, La) have shown that the formation of La–O–Al bonds results in a modification of the electronic structure of both the aluminum and lanthanum cations. This modification alters the acid–base properties of the catalyst surface (13). Since for the case of supported or mixed oxide catalysts the estimate of basicity has to be carried out, these charge transfer process can be considered.

In the present work we have shown that the UV–vis spectrum of a solid provides evidence of the position and donating properties of the top of the valence band and so can be used as a measure of the basicity of the solid.

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