THE POISONING EFFECT OF Co_3O_4 ON γ-Al_2O_3 AND MgO SUPPORTS DURING THE DECOMPOSITION OF ISOPROPYL ALCOHOL

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Catalysts containing 20 wt.% Co_3O_4 supported on γ-Al_2O_3 and MgO were prepared. The catalyst precursors were analyzed by TG, DTG and DTA, and the calcined catalysts (400–700 °C) were characterized by XRD. The amount of excess surface oxygen for the catalysts was estimated iodometrically. The vapour-phase decomposition of isopropyl alcohol over these catalysts was studied. Co_3O_4/γ-Al_2O_3 catalysts are selective towards propene formation, whereas Co_3O_4/MgO catalysts are selective towards acetone formation. The poisoning effect of Co_3O_4 on both supports and the activity of the catalysts is discussed.

Cobalt oxide catalysts are currently used in petrochemical hydrodesulfurization processes[1] and in the partial oxidation of alkenes[2]. Supported or mixed Co_3O_4/Al_2O_3 catalysts have also been used in the decomposition of H_2O_2 (ref.[3]). A few papers have been devoted to the characterization of cobalt oxide/supported catalysts[4,5]. Co_3O_4/MgO catalysts have been used in various chemical reactions such as the oxidation of propene[6]. Adsorption of O_2, NO_2 and NO on CoO–MgO catalysts[7] has been reported. Many characterization studies have been made on magnesia supports[8], MgO–CoO solid solution[9] and metal ions/MgO catalysts[10].

The present work deals with the poisoning effect of Co_3O_4 on two supports, γ-Al_2O_3 and MgO, during the decomposition of isopropyl alcohol.

EXPERIMENTAL

Materials and Techniques

The γ-Al_2O_3 support was prepared following Murgulescu et al.[11] from aluminium hydroxide $Al(OH)_3$ precipitated by the reaction of $AlCl_3$ (BDH, U.K.) with NH_4OH. The substance was then calcined at 750 °C in air for 10 h. The MgO support was prepared by direct calcination of $MgCO_3$ (Prolabo, France) in air at 900 °C for 4 h. The catalyst samples containing 20 wt.% Co_3O_4 supported on γ-Al_2O_3 and MgO, respectively, were prepared as follows: 18.13 g of $Co(NO_3)_2 \cdot 6\,H_2O$ (BDH, U.K.) was dissolved in 50 ml of deionized water and 20 g of the support (γ-Al_2O_3 or MgO) was suspended in the solution. The mixtures were evaporated to dryness over a water bath with continuous stirring. The resulting materials were dried overnight, in an oven at 120 °C and finally calcined in air for 5 h at 400–700 °C.

Thermal analyses (i.e. thermogravimetry (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA)) were carried out by the conventional methods described elsewhere[12]. X-Ray powder diffractograms were obtained on a JSX-60 X-ray diffractometer (JEOL, Japan) equipped with a Zr-filtered MoKα radiation source (λ = 0.7093 Å). Excess surface oxygen for the catalysts under investigation was determined iodometrically in acidic medium[13]. Measurements of the catalytic activity and selectivity of the catalysts towards the decomposition of isopropyl alcohol (IP) were conducted in the continuous flow mode at atmospheric pressure. A mixture of 1.4% IP in N_2, obtained by passing the carrier gas through liquid IP held at 3 °C, was used. The total flow rate was kept constant at 215 ml/min. Catalyst sample (0.5 g) in a glass reactor 16.5 cm long, 1 cm i.d., was stabilized for 2 h at 190 °C before measurement. The feed exit gases were analyzed by gas chromatography (Shimadzu GC-14A, equipped with a Shimadzu Chromatopac C-R4AD data processor) using a stainless steel column (PEG 20M 20% on Chromosorb W, 60/80 mesh, 3 m × 3 mm) at 110 °C. Catalytic activity was expressed as the degree of conversion of supplied IP to all products, and selectivity as the mole ratio of a particular product in all decomposition products, respectively. The reaction rates and reaction order were calculated as described elsewhere[14].

Surface area measurements of the samples were carried out by the BET method[15] with N_2 as the adsorbate, by using a conventional volumetric gas adsorption apparatus[16]. The basicity of the Co_3O_4/MgO catalysts was determined by investigating the adsorption of acetic acid molecules by the pulse method[17]. An amount of 0.5 g of each catalyst was accommodated in the reactor at the reaction temperature. Pulses of a heptane solution of 0.1 M acetic acid (10 μl) were injected into the sample followed, after one minute, by passing the flow of IP. The concentration of unreacted IP was calculated after each injection and the pulses were stopped when the adsorbate (acetic acid) peak appeared in the chromatogram. The number of pulses characterized the basicity of each catalyst. Similarly, the acidity of the $Co_3O_4/\gamma\text{-}Al_2O_3$ catalysts was determined by examining the adsorption of pyridine.

RESULTS AND DISCUSSION

Thermal Analyses

TGA, DTG and DTA curves of the 20 wt.% $Co_3O_4/\gamma\text{-}Al_2O_3$ precursor are shown in Fig. 1*a*. The TGA curve exhibits two overlapping weight loss steps between 75–179 °C, followed by a third step between 179–231 °C, with a total weight loss of 30.9% of the initial sample weight. The DTG curve of this sample displays three peaks with T_{max} at 92, 135 and 198 °C corresponding to the three steps in the TGA curve. In the DTA of the $Co_3O_4/\gamma\text{-}Al_2O_3$ precursor, there are three endothermic peaks located at 90, 133 and 196 °C due to the dehydration and decomposition of cobalt nitrate supported on $\gamma\text{-}Al_2O_3$ (refs[18,19]). The TGA curve of the 20 wt.% Co_3O_4/MgO precursor (Fig. 1*b*) shows one step within the temperature range of 320–390 °C, associated with a weight loss of 37.5% of the initial sample. The DTA curve of this sample exhibits a peak at 379 °C with a shoulder at 349 °C. The DTA curve (Fig. 1*b*) shows a large split endotherm with T_{max} at 366 and 378 °C, corresponding to the dehydration and decomposition processes of cobalt nitrate and formation of Co_3O_4 on MgO. The activation energies (ΔE) for the thermal decomposition of the two precursors (nitrates) were calculated from the TGA data using the Coats–Redfern equation[20] as explained elsewhere[21]. The values obtained are $\Delta E = 63.1 \pm 0.6$ and 86.2 ± 6.1 kJ/mol for the two decomposition steps of γ-Al_2O_3 supported Co(II) nitrate, and $\Delta E = 218.3 \pm 8.7$ kJ/mol for MgO supported Co(II) nitrate (in a good agreement with the values found for pure cobalt nitrate[22]).

X-Ray Diffraction Analysis

XRD diffractograms of Co_3O_4/γ-Al_2O_3, calcined at 400–700 °C for 5 h in air (Fig. 2*a*) agree well with published values for both γ-Al_2O_3 (ASTM 10-425) and Co_3O_4 (ASTM 9-418). They consist of lines related to the γ-Al_2O_3 support (d = 2.406, 1.985 and 1.413 Å; ref.[23]) and lines belonging to Co_3O_4 (d = 2.804 and 1.539 Å; ref.[24]). The XRD patterns of the Co_3O_4/MgO catalyst calcined in air for 5 h are shown in Fig. 2*b*. The diffraction lines are consistent with published data for MgO (ASTM 4-0829), Co_3O_4 (ASTM 9-418) and the (Co,Mg)O system (ASTM 2-1201). The lines at d = 1.216, 1.487 and 2.105 Å are due to the MgO support[25], whereas those at d = 0.942, 1.055 and 2.431 Å are attributed to Co_3O_4 (ref.[24]). The line at d = 1.267 Å (with an intensity of 6%) is ascribed

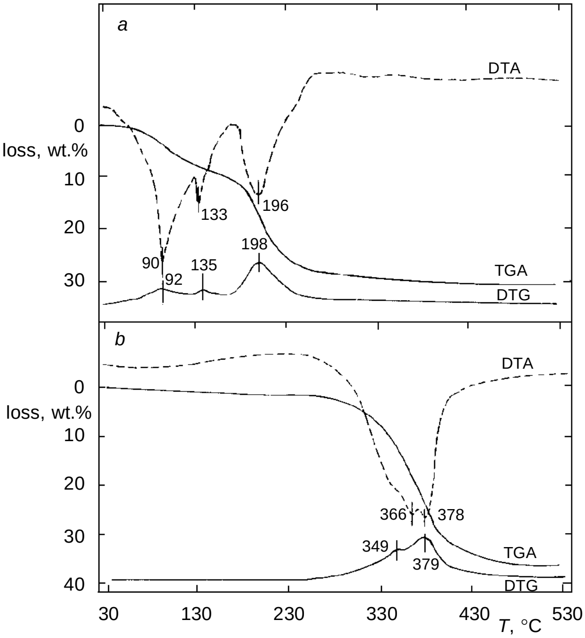

FIG. 1
TGA, DTG and DTA curves of the thermal decomposition of *a* 20 wt.% Co_3O_4/γ-Al_2O_3, *b* 20 wt.% Co_3O_4/MgO precursors, carried out at 10 °C/min in a dynamic atmosphere of dry N_2 (40 ml/min)

to the formation of a new (Co,Mg)O phase (ASTM 2-1201). From the above results of XRD analysis it can be concluded that Co_3O_4 does not react with γ-Al_2O_3 within the temperature range of 400–700 °C, whereas it partially reacts with the support forming (Co,Mg)O.

Catalytic Activity Measurements

It should be noted that the γ-Al_2O_3 and MgO supports used in the present study were calcined at temperatures higher than the calcination temperatures of the supported Co_3O_4 oxide catalysts (e.g. γ-Al_2O_3 was originally calcined at 750 °C while the MgO support was calcined at 900 °C). Hence, it is reasonable to assume that neither of the supports in the Co_3O_4/γ-Al_2O_3 and Co_3O_4/MgO systems suffered any change during the calcination of the systems from 400–700 °C. Consequently, all changes in the catalytic activity of the supported catalysts can be attributed to Co_3O_4 rather than to γ-Al_2O_3 or MgO.

a) Over Co_3O_4/γ-Al_2O_3 *catalysts:* γ-Al_2O_3 oxide is known to possess Lewis type acidity which arises during its preparation from $Al(OH)_3$ (ref.[26]). The activated alumina can be rehydrated by water formed during the reaction[27]. Therefore, the pure γ-Al_2O_3 support exhibits a very high catalytic activity and selectivity towards the dehydration reaction of IP (to produce propene), see Table I.

The addition of Co_3O_4 (which is known to possess both acidic and basic properties) to γ-Al_2O_3 generally resulted in a reduction of the activity of γ-Al_2O_3 (Table I). The catalytic activity of the four Co_3O_4/γ-Al_2O_3 catalysts increased from 400 °C to reach a

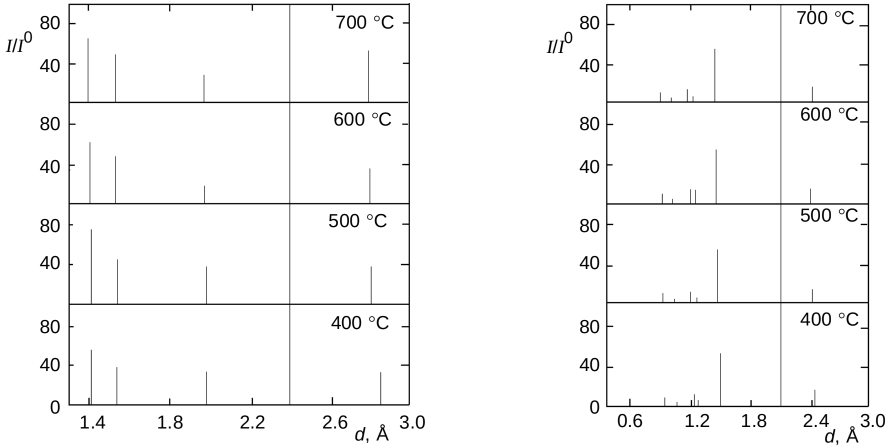

FIG. 2

XRD patterns of *a* 20 wt.% Co_3O_4/γ-Al_2O_3, *b* 20 wt.% Co_3O_4/MgO, calcined at different temperatures for 5 h in air maximum at 600 °C. Subsequently, the catalytic activity decreased at 700 °C. This trend could be correlated with surface excess charge data and acidity measurements (Table I).

The catalytic activity measurements give evidence that cobalt oxide blocks the active centres of γ-Al_2O_3, thus reducing its activity while having no effect on the support selectivity. Hence, the catalyst centres presumably form on alumina domains but not on cobalt oxide domains.

b) Over Co_3O_4/MgO catalysts: The pure basic MgO oxide support is observed to possess a very high catalytic activity and selectivity towards the dehydrogenation reaction of IP (to produce acetone), see Table I.

The addition of Co_3O_4 to MgO resulted in a general decrease in the catalytic activity of the pure MgO support. The catalytic activity was found to be inversely proportional to the calcination temperature. This behaviour could be correlated with the values of their excess surface charge and basicity measurements (Table I). Similarly, the change in the catalytic activity could be attributed to Co_3O_4 rather than to MgO support be-

TABLE I

Results of decomposition of isopropyl alcohol over Co_3O_4/γ-Al_2O_3 and Co_3O_4/MgO catalysts at different calcination temperatures (in °C). All catalysts were calcined in air for 5h

Parameter	Catalyst									
	γ-Al_2O_3 support	20 wt.% Co_3O_4/γ-Al_2O_3				MgO support	20 wt.% Co_3O_4/MgO			
		400	500	600	700		400	500	600	700
Conversion, %	99.3	27.0	56.4	61.9	57.5	99.9	12.0	4.9	2.7	0.9
R_{TP}	611.6	169.7	347.3	381.2	354.1	614.5	73.3	30.0	16.9	5.6
R_p	610.9	89.5	345.2	380.8	353.5	1.2	–	–	–	–
R_a	0.7	78.7	2.1	0.3	0.7	613.2	73.3	30.0	16.9	5.6
S_p	99.88	53.6	99.4	99.9	99.8	0.2	–	–	–	–
S_a	0.11	46.4	0.6	0.1	0.2	99.8	100	100	100	100
O_{ex}, atom% . 10^{-3}	–	2.6	3.1	9.8	1.8	–	46.3	34.3	12.2	2.6
S_{BET}, m^2/g	42	60.4	61.8	61.1	60.5	15	38.1	32.3	23.8	16.2
Acidity[a]	4.8	1.7	2.9	3.4	1.9	–	–	–	–	–
Basicity[a]	–	–	–	–	–	69.3	24	22	18	3

R_{IP} the total rate of removal of IP (mmol/h g cat.), R_p the rate of formation of propene (mmol/h g cat), R_a the rate of formation of acetone (mmol/h g cat.), S_p the selectivity towards the formation of propene, S_a the selectivity towards the formation of acetone, O_{ex} the excess surface oxygen.

[a] Acidity and basicity are expressed as $mmol/m^2_{cat} . 10^{-3}$.

cause MgO was initially calcined at 900 °C, i.e. much higher than the calcination temperature of all the four catalysts.

The catalytic activity measurements (Table I) demonstrate that the poisoning effect of Co_3O_4 on the MgO support is twice as large as on γ-Al_2O_3. For example, Co_3O_4/MgO calcined at 400 °C reduced the catalytic activity to about 1/8 with respect to that of the pure MgO; at the same calcination temperature, Co_3O_4/γ-Al_2O_3 reduced the catalytic activity of pure γ-Al_2O_3 to about 1/4 of its initial value.

The surface excess charges seem to be more effective in case of the Co_3O_4/MgO catalysts as compared to the Co_3O_4/γ-Al_2O_3 system.

The activation energies for the dehydration of IP over Co_3O_4/γ-Al_2O_3 and over Co_3O_4/MgO, both at 500 °C, were calculated to be 81.3 ± 3.4 and 77.5 ± 9.1 kJ/mol, respectively, with the reaction order $n = 0.24$ and 0.26, respectively.

Finally, the catalytic activity of pure Co_3O_4 is known to be influenced by the calcination temperature, e.g. in the decomposition of H_2O_2 (ref.^{28}). Therefore, the effect of calcination temperature of pure Co_3O_4 on its catalytic activity during the decomposition of IP will be dealt with in a separate study.

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