

Effect of Calcination Temperature and Chemical Composition on Catalytical Activity of Co_3O_4 Supported on $\gamma\text{-Al}_2\text{O}_3$

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Summary: Cobalt/aluminium mixed oxides of varying compositions (0.05 to 0.2 $\text{Co}_3\text{O}_4\text{:Al}_2\text{O}_3$) were prepared by impregnating finely powdered poorly crystalline gamma-alumina with different proportions of cobalt nitrate using a pore-filling method. The prepared solids were dried at 100°C then calcined at $450\text{-}900^\circ\text{C}$. The catalytic activities of different supported solids were determined using the catalytic oxidation of CO with O_2 at $80\text{-}300^\circ\text{C}$ by these mixed oxides. The apparent activation energies (ΔE) of the catalytic reaction were determined for each catalyst from the data of first-order reaction rate constant (k) measured at different reaction temperatures for various solids precalcined at different temperatures.

The results obtained revealed that the catalytic activity increases progressively by increasing the amount of cobalt oxide in each catalyst and decreases by increasing the precalcination temperature of various solids. Furthermore, ΔE increases slightly by increasing the roasting temperature of the employed catalysts from 450 to 650°C then increases suddenly for all solids precalcined at 750°C . The computed ΔE values for different catalysts preheated at 750°C were 28, 25.5, 21.5 and 12.2 k.cal/mol for Al_2O_3 specimens treated with 0.05, 0.1, 0.15 and 0.2 mol Co_3O_4 , respectively. These results indicate that Co_3O_4 is the most catalytically active constituent of the mixed oxides and the catalysis of CO oxidation, on different solids roasted at $450\text{-}650^\circ\text{C}$, proceeds according to a mechanism different from that dominating in case of the solids roasted at 750°C .

Introduction

Cobaltic oxide (Co_3O_4) prepared by the thermal decomposition of cobalt hydroxide or basic cobalt carbonate in air at temperatures below 900°C is devoted with high catalytic activity with respect to the oxidation of CO[1-5]. The Li-doping of Co_3O_4 catalyst has been found to much decrease its activity in CO oxidation with subsequent increase in the apparent activation energy (ΔE) of the catalyzed reaction[6]. This drop in the activity of Li-doped solid has been attributed to the blocking of some of the cobalt ions, involved in the catalysis of CO oxidation, by oxygen anions (incorporated O^{2-}). These O^{2-} anions, formed in case of doped solid would not interact easily with CO at

temperatures below 250°C [6]. The effects of supporting cobaltic oxide on an active carrier such as $\gamma\text{-Al}_2\text{O}_3$ on the surface properties of supported catalyst have been extensively studied using modern surface-sensitive techniques such XPS, ISS and DRS[7-10]. The influence of $\gamma\text{-Al}_2\text{O}_3$ support on the catalytic activity of $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ solids received much less importance.

We have investigated the effects of supporting cobaltic oxide on an active $\gamma\text{-Al}_2\text{O}_3$ on the catalytic activity of the produced solids. The catalytic oxidation of CO with O_2 at different temperatures by supported catalysts was carried out. The influence

of both Co_3O_4 content and calcination temperature on the catalytic activities of various solids has been studied.

Experimental

Preparation of catalysts

Cobalt/aluminium mixed-oxides of varying compositions were prepared by impregnating finely powdered poorly crystalline $\gamma\text{-Al}_2\text{O}_3$ with different proportions of cobalt nitrate solution. The impregnated alumina specimens were then dried at 100°C and calcined at different temperatures between 450 and 900°C . The nominal compositions of the prepared catalysts were $0.05 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$, $0.1 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$, $0.15 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$ and $0.2 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$. The extents of cobalt oxide in these solids are 10.5, 19.1, 26.1 and 32.1 wt.% Co_3O_4 , respectively.

Techniques

X-ray investigations of the calcined supported catalysts were performed with a Philips diffractometer (type PW 1390). The patterns were obtained with iron-filtered cobalt radiation ($\lambda = 1.7889\text{\AA}$) at 30 kV and 10 mA with a scanning speed of 2° in $2\theta \text{ min}^{-1}$.

The catalytic oxidation of CO with O_2 on various catalysts was carried out at temperatures between 80 and 300°C using a static method. A stoichiometric mixture of CO and O_2 at a pressure of 2 Torr was used. A fresh catalyst sample of 200 mg was employed for each kinetic experiment.

Results and Discussion

X-ray investigation of the supported catalysts:

The characteristic diffraction lines of well-crystallized Co_3O_4 phase were only detected in the patterns of the various prepared solids precalcined at $450\text{--}900^\circ\text{C}$ except the sample having the composition $0.1 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$. This latter solid, being calcined at 850 and 900°C , the diffraction lines of both CoAl_2O_4 and Co_3O_4 phases were observed in its patterns. A calcination temperature of 1000°C was necessary for the formation of crystallized CoAl_2O_4 phase in case of $0.15 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$ and $0.2 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$ solids. Preliminary experiments

showed that the thermal treatment of an additional sample, containing more cobalt oxide than the prepared solids ($0.33 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$, at 1000°C did not result in the formation of CoAl_2O_4 . These results clearly indicate that the solid-solid interaction between cobalt and aluminium oxides to yield massive crystallized cobalt aluminate depends mainly on both extent of Co_3O_4 and calcination temperature. The formation of CoAl_2O_4 is favoured by increasing the calcination temperature of mixed oxide solids and/or by decreasing the extent of Co_3O_4 present. This conclusion is evidenced by the results published by some authors[7,10,11]. The massive formation of cobalt aluminate requires relatively high temperatures while the production of this compound on the outermost surface layers of mixed-oxide solids takes place at much lower temperatures[12]. In fact, it has been reported by XPS measurements that CoAl_2O_4 exists on the surface of mixed oxides precalcined at temperatures starting from 450°C [13,14].

Catalytic activities of Co/Al-mixed oxides:

The catalytic activities of various solids were determined using the catalytic oxidation of CO with O_2 by these catalysts. The catalytic reaction was carried out at temperatures between 80 and 300°C depending on both the composition of each catalyst and its precalcination temperature. First-order kinetics were observed in all cases. Figures 1 and 2 show representative first-order plots of CO oxidation on $0.05 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$ and $0.2 \text{ Co}_3\text{O}_4:\text{Al}_2\text{O}_3$ solids calcined at 450 and 750°C . The reaction rate constants(k), slopes of first-order plots, are determined at different reaction temperatures for each catalyst calcined at various temperatures. The data of k at different reaction temperatures enabled the calculation of apparent activation energies of the catalytic reaction (ΔE) for the various catalysts through a direct application of the Arrhenius equation. The effects of Co_3O_4 content and calcination temperature of mixed oxide catalysts on their catalytic activities are better illustrated in figure 3 which represents the specific reaction rate constant, k, (reaction rate constant per unit surface area) as a function of Co_3O_4 content for the catalytic reaction carried out at $130\text{--}200^\circ\text{C}$ on different solids precalcined at 450 and 650°C . It can be observed from figure 3 that the activities of various supported solids increase progressively by increasing the amount of cobalt oxide in these catalysts. These results indi-

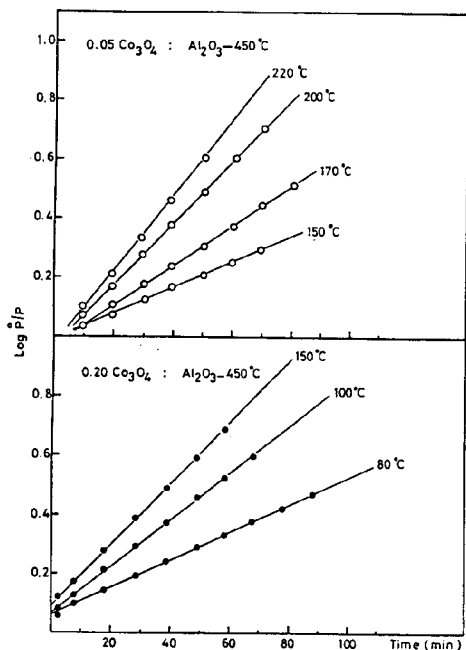


Fig. 1: First-order plots of CO oxidation at different temperatures on various catalysts precalcined at 450°C.

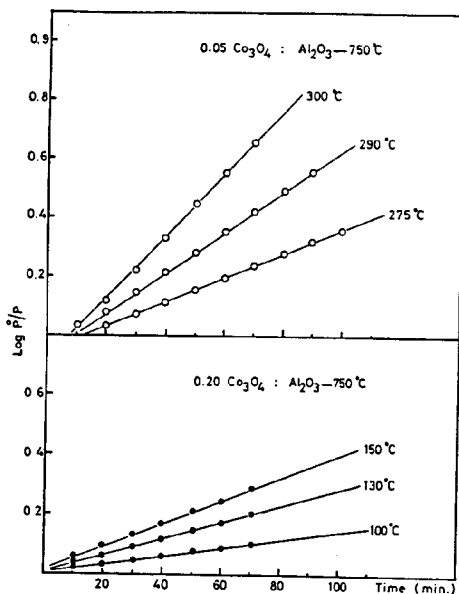


Fig. 2: First-order plots of CO oxidation at different temperatures on various catalysts precalcined at 750°C.

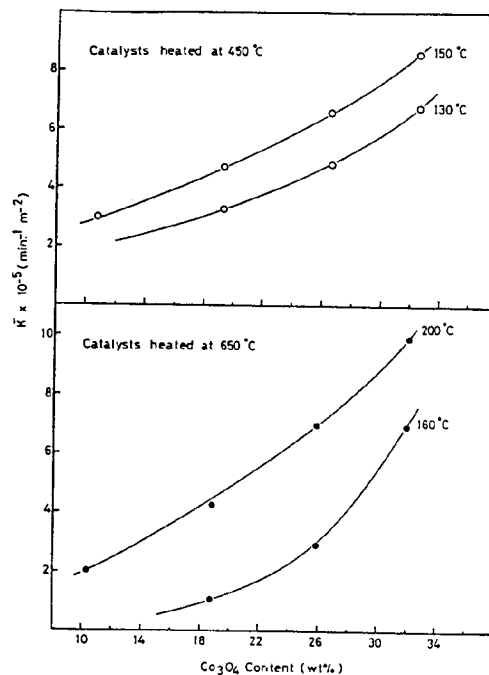


Fig. 3: Relationship between k (reaction rate constant per unit surface area) and extent of Co_3O_4 in different catalysts.

cate that Co_3O_4 represents the most catalytically active constituent of different cobalt/aluminium mixed-oxides. The curves relating k and Co_3O_4 content are of increasing slopes. This indicates that the specific catalytic activity per unit mass of Co_3O_4 (k per 1 g of Co_3O_4 in mixed oxide catalysts) increases by increasing the amount of cobalt oxide in each catalyst. This finding might show that the increase in the extent of Co_3O_4 leads to the formation of cobalt species of higher catalytic activity than that of cobalt species formed at lower cobalt oxide content. It has been shown by X-ray investigation[13] that cobalt exists in the form of divalent cobalt cations located in octa and tetrahedral sites of $\gamma\text{-Al}_2\text{O}_3$ lattice when the percentage loading is smaller than 10 wt. cobalt and above this limit cobalt exists in the form of Co_3O_4 . It is known that Co_3O_4 is devoted with the highest catalytic activity as compared with the other cobalt species[9]. On this basis, the observed increasing slopes of the curves relating the specific catalytic activity (k) and the

concentration of cobalt oxide in each catalyst specimen can be attributed to the progressive formation of cobalt oxide phase by increasing the amount of cobalt nitrate added to the employed alumina support.

The apparent activation energies of CO oxidation (ΔE) were determined for different solids precalcined at temperatures in the range 450-900°C. The computed ΔE values are given in Table 1. It can be seen from this table that ΔE suffers progressive slight increase, for most of the catalysts, by increasing their calcination temperature in the range 450-650°C then suffers a sudden increase (about 2-fold) at precalcination temperatures equal to or higher than 750°C. These results clearly indicate that the catalysis of CO oxidation reaction proceeds on each catalyst sample according to almost the same mechanism when these catalysts are precalcined at temperatures in the range 450-650°C. And the catalytic reaction takes place via another mechanism(s) over the catalysts precalcined at temperatures above this limit. Table 1 shows also that the maximum values of ΔE are 28.2, 25.5, 21.5 and 12.2 k.cal/mol for alumina specimens pretreated with 10.5, 19.1, 26.1 and 32.1 wt.% Co_3O_4 , respectively. It has been reported that the maximum value of ΔE for CO oxidation with O_2 by pure and Li-doped Co_3O_4 catalysts[5,6] is smaller than 15 k.cal/mol. The ΔE values of CO oxidation by cobaltic oxide supported on $\gamma\text{-Al}_2\text{O}_3$ and precalcined at 450-650°C (Table 1) correspond to the oxidation of CO catalyzed by Co_3O_4 . Moreover, the computed values of ΔE for the supported catalysts preheated at temperatures $> 750^\circ\text{C}$ stand for the oxidation reaction catalyzed by cobalt species of smaller catalytic activity than that of cobaltic oxide. These species are more probably cobalt aluminate. In fact, it has been reported that Co_3O_4 interacts at about 650°C with Al_2O_3 on the uppermost surface layers of mixed oxide catalysts to produce cobalt aluminate[10-12]. Indeed, CoAl_2O_4 , is devoted with catalytic activity smaller than that of Co_3O_4 especially for oxidation-reduction and sulfurization reactions[9]. It can be noticed from table 1 that ΔE attains a maximum value of 12.2 k.cal/mol for the catalyst specimen containing 32.1 wt.% cobalt oxide and precalcined at 900°C which suggests that the catalytic reaction, carried out on this solid, is catalyzed by Co_3O_4 and not by CoAl_2O_4 . In fact, X-ray investigation previously given in this work, revealed that alumina specimen pretreated with

32.1 wt.% cobaltic oxide and preheated at 900°C was constituted entirely of well-crystallized Co_3O_4 phase.

Table 1: Effect of catalyst composition and calcination temperhe magnitudes of the apparent activation energixidation

Catalyst	Calcination Temperature (°C)	ΔE Kcal/mole	Range of Temperature °C
0.05 $\text{Co}_3\text{O}_4:\text{Al}_2\text{O}_3$	450	5.3	150-250
	550	5.9	250-300
	650	7.6	250-300
	750	28	275-300
0.1 $\text{Co}_3\text{O}_4:\text{Al}_2\text{O}_3$	450	7.1	110-170
	550	11.1	140-200
	650	19.8	170-220
	750	25.5	170-210
0.15 $\text{Co}_3\text{O}_4:\text{Al}_2\text{O}_3$	450	10.3	80-160
	550	2.8	130-200
	650	9.9	160-200
	750	21.5	140-180
0.2 $\text{Co}_3\text{O}_4:\text{Al}_2\text{O}_3$	450	3.4	80-150
	550	6.5	85-200
	650	6.2	70-200
	750	11.9	100-200
	900	12.2	145-220

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