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EFFECT OF DOPING METHOD OF V_2O_5 ON Co_3O_4/TiO_2 SUPPORTED CATALYST CHARACTERISTICS

Hassan, S. A., Mekewi, M. A. and Sadek, S. A.
Chemistry dept., Faculty of Science, Ain-Shams Univ.
Abbassia. Cairo. Egypt.

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ABSTRACT

Investigation of V_2O_5-doped Co_3O_4/TiO_2 catalyst system as a function of method of doping was carried out. It was found that doping with the surface coating method of the oxide system lead to a marked change in the chemistry of the active Co_3O_4 phase. This was reflected on the surface characteristics, specific activity with a pronounced decrease in the extracted species and also on H_2-chemisorption behaviour. Doping by codispersion method lead to a system close in behaviour to the original undoped Co_3O_4/TiO_2 in its main characteristics. Yet some differences are assigned in the corresponding specific activity.

1. INTRODUCTION

Effect of preparational parameters on structure and activity of supported Co_3O_4/TiO_2 in addition to the nature of the active phases are reported (1-3). The dissolution mechanism of V_2O_5 and MoO_3; as dopants; in the Co_3O_4 lattice and the after effects on the chemistry of the active species was also proposed (4). However, doping of such prospective

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Co_3O_4/TiO_2 hydrocracking catalyst by V_2O_5 and its overall properties is seriously lacking in literature. The present study was undertaken to investigate the effect of doping method by V_2O_5 on the major characteristics of the catalyst system, namely Co_3O_4/TiO_2 and the nature of the active species in respect.

2. Experimental techniques:

2.1 Catalyst

Two methods of doping are adopted for the preparation of the doped catalysts, with Co_3O_4 = 3.8 mole% and V_2O_5 coating, prepared as follow:

2.1.1 Surface coating method:

This method was carried out by impregnating the already prepared Co_3O_4/TiO_2 (5); designated as **CT**; in the appropriate concentration of NH_4VO_3. The mixture was subjected to stirring for 10 hours until a homogeneous paste was obtained. The paste was then dried at 110 ^{0}C for 13 hours and finally calcined in air at 330 ^{0}C for 5 hours. This doped sample is designated as **CTV I**.

2.1.2 Co-dispersion method:

Co-dispersion of both Co_3O_4 and V_2O_5 phases on the titania support [supplied by BDH] was carried out by impregnating the dried sample of TiO_2 in a mixture of NH_4VO_3

and $Co(NO_3)$ solution [supplied by BDH] of the appropriate concentrations while stirring. The mixture was filtered and then dried at 110 ^0C for 24 hours. The product was finally calcined in air at 330 ^0C for 5 hours. The catalyst prepared by this method is referred to as CTV II.

2.3 Infrared study

Infrared absorption spectra were carried out for solid structure confirmation using a Pye-Unicam spectrophotometer, model SP-200.

2.4 Texture and pore structure:

Adsorption-desorption isotherms of pure N_2 gas were performed at 77 ^0K using a corrected volumetric apparatus (6). Specific surface areas (S_{BET}), average pore radius (r) and porosity investigations were calculated using the BET equation model and n_S - n_R plots respectively (7, 8).

2.5 Dissolution of surface active species:

As the degree of deactivation seems to depend entirely on the fraction dissolved of surface active species (9) so determination of surface active species will be useful. The surface active species were identified through the dissolution by hydrochloric acid (pH=2) which was added to 100 gram solid catalyst sample and then shaken for 3 hours. The specific activity of the solid catalysts was estimated through the use of H_2O_2 decomposition model (5) referred to as $(a)_{extr}$.

2.6 Hydrogen chemisorption:

A standard pretreatment of catalyst samples was adopted through the course of this investigation which involves outgassing at room temperature for 2 hours then heating at 330^0C for 1 hour at pressure of 10^{-5} torr. Adsorption isotherms of pure hydrogen were measured at 330 ^0C in pressure range up to 200 torr (1st isotherm), using a conventional volumetric apparatus. After the first adsorption isotherm was completed, the catalyst samples were then outgassed once more at 330 ^0C and the second isotherm was carried out in the same previous manner.

3. RESULTS AND DISCUSSION

3.1 XRD analysis:

The XRD pattern of the unsupported cobalt oxide treated under the same preparational conditions as those of the supported catalysts indicated a match to that of Co_3O_4 of fcc shape at d=0.467, 0.286, 0.156 and 0.143 nm. Pure Titania support was also investigated to assess which type is dealt with. The XRD analysis proved the existence of Anatase type from tetragonal shape at d=0.352, 0.238, 0.189, 0.167, 0.148 and 0.126 nm. All undoped and V_2O_5 doped samples showed mainly the pattern of the Titania support with additional diffracted lines at d=0.244 nm, which is the most intensive of the Co_3O_4

phase. Effect of dopant (V_2O_5 phase) on the overall crystallinity was not at all observed, figure 1.

3.2 Infrared study:

The infrared spectral analysis for cobalt nitrate samples before and after calcination to cobalt oxide proved the disappearance of the nitrate distinguished peak. This result justify the use of 330 ^{0}C as the calcination temperature, figure 2.

3.3 Texture and pore structure:

The adsorption-desorption isotherm of pure TiO_2 support was found almost reversible, whereas, undoped and V_2O_5 doped Co_3O_4/TiO_2 samples showed marked hysteresis, shape of which changes with the method of doping, figure 3. The specific surface area values, table 1, shows that the value of Co_3O_4/TiO_2 is slightly higher than that of pure Co_3O_4 which indicates more or less a monolayer coverage of the supported system. Upon doping the specific surface area seems to increase markedly for both samples CTV I and CTV II as a probable cause of developing new pore system. Such influence of surface area increase upon doping has shown relevant changes of other solids characteristics as will be observed hereafter. Figure 4, illustrates porosity results based on applying the n_S-n_R method (8, 10). The results indicate a general mesoporous structure for the samples CT (still with the same value of r as of pure Co_3O_4) and CTV I while CTV II shows slight increase towards more mesoporous nature, i. e increase of narrower pores fraction. It may be concluded, therefore, that the increase in the surface area values for doped samples seem to proceed along widely different regimes: doping through surface coating (CTV I) develops new chemically interacted phases between V_2O_5 and Co_3O_4 of well developed surface area, whereas, doping by co-dispersion (CTV II) develops more mesoporous system.

3.4 Dissolution of active species:

The interacted fraction of Co species in the sample CT; referred to as Co-t which is occupying the tetrahedral sittings of the support; are demonstrated in table 2. This fraction by itself is an indication of support (TiO_2) stabilization to the Co^{2+} species most probably through its anion vacancies (11). Expectedly such fraction is shown to increase markedly for sample CTV I, where an electron transfer might have been encouraged through the interaction between V_2O_5 and Co_3O_4. On the other hand sample CTV II showed no marked change in that interacted fraction value which might lead to suggest that the dopant in this case is existing in a proper dispersed state as being independent of the Co_3O_4 phase, with no distinguishing effect on its chemistry. The H_2O_2 decomposition results; as a reference for specific activity; runs exactly along the same routine as of the dissolution data

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with CTV I showing most activity.

3.5 Hydrogen chemisorption:

The temperature of 330 ^{0}C was chosen to carry out the hydrogen chemisorption procedure as being high enough to detect the strong metal-support interaction (SMSI) and at the same time is low enough to avoid both sintering and the conversion of the TiO_2 support type Anatase to Rutile. Figure 5, illustrates H_2 adsorption isotherms for various samples. Extremely small uptake of hydrogen at 330 ^{0}C seems to be the case for the titania support, which again runs in agreement with Smith results (12), the isotherm represents most likely an activated adsorption as the reversible isotherm gives no adsorption results. In obvious contrast, the H_2-adsorption isotherm on pure Co_3O_4 at 330 ^{0}C profiled a multistage adsorption behaviour which seems to correspond to the different oxidation states of cobalt with a highly reversible character (3), figure 5, b. The irreversible H_2-uptake estimated from the difference between the two isotherms corresponding to 0.67 m mole H_2/g at monolayer coverage coming entirely from the supported cobalt oxide phase. Pure TiO_2 support shows only very little or no adsorption at all at this temperature, i.e 330 ^{0}C.

Total H_2-adsorption isotherms of samples CTV I and CTV II are shown in figure 6. From the figure, it seems that the isotherms suffer some suppression upon doping, which may be attributed to the dissolution of V_2O_5 into the Co_3O_4 lattice and/or electron transfer from V_2O_5 to Co_3O_4 each related to either method of doping.

It could be concluded generally that for doped sample **CTV** I, the substitution mechanism seems to predominate leading to some shrinkage of the Co_3O_4 lattice being reflected on the chemistry of the produced structure. On the other hand, the electronic factors seems more significant when dealing with sample **CTV** II.

CONCLUSION

The behaviour of supported catalyst system of Co_3O_4/TiO_2 when doped with V_2O_5 depends on the method of doping whether is surface coated or codispersed. Doping by codispersion did not affect much the main characteristics of the solid catalyst system despite the fact that the specific activity slightly increased. Meanwhile, doping by the surface coating method had a direct effect on most of the major aspects of the system with regard to surface features, nature of reactive species and specific activity towards the decomposition of the H_2O_2 reaction model. Reasons of varying effects of doping method were made attributed to either modification to the system chemistry or due to electronic factors.

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Table 1.

SOLID DESIGNATION	$S_{BET.}$ m^2g^{-1}	$\bar{r}$ A°
Pure Co_3O_4	113.2	23
Pure TiO_2	98.9	23
Supported Co_3O_4/TiO_2 (CT)	111.3	23
V_2O_5 doped Co_3O_4/TiO_2 (CTV I)	130.5	33
V_2O_5 doped Co_3O_4/TiO_2 (CVT II)	123.5	40

Specific surface areas (S_{BET}) and average pore radius ($\bar{r}$) values of catalyst samples

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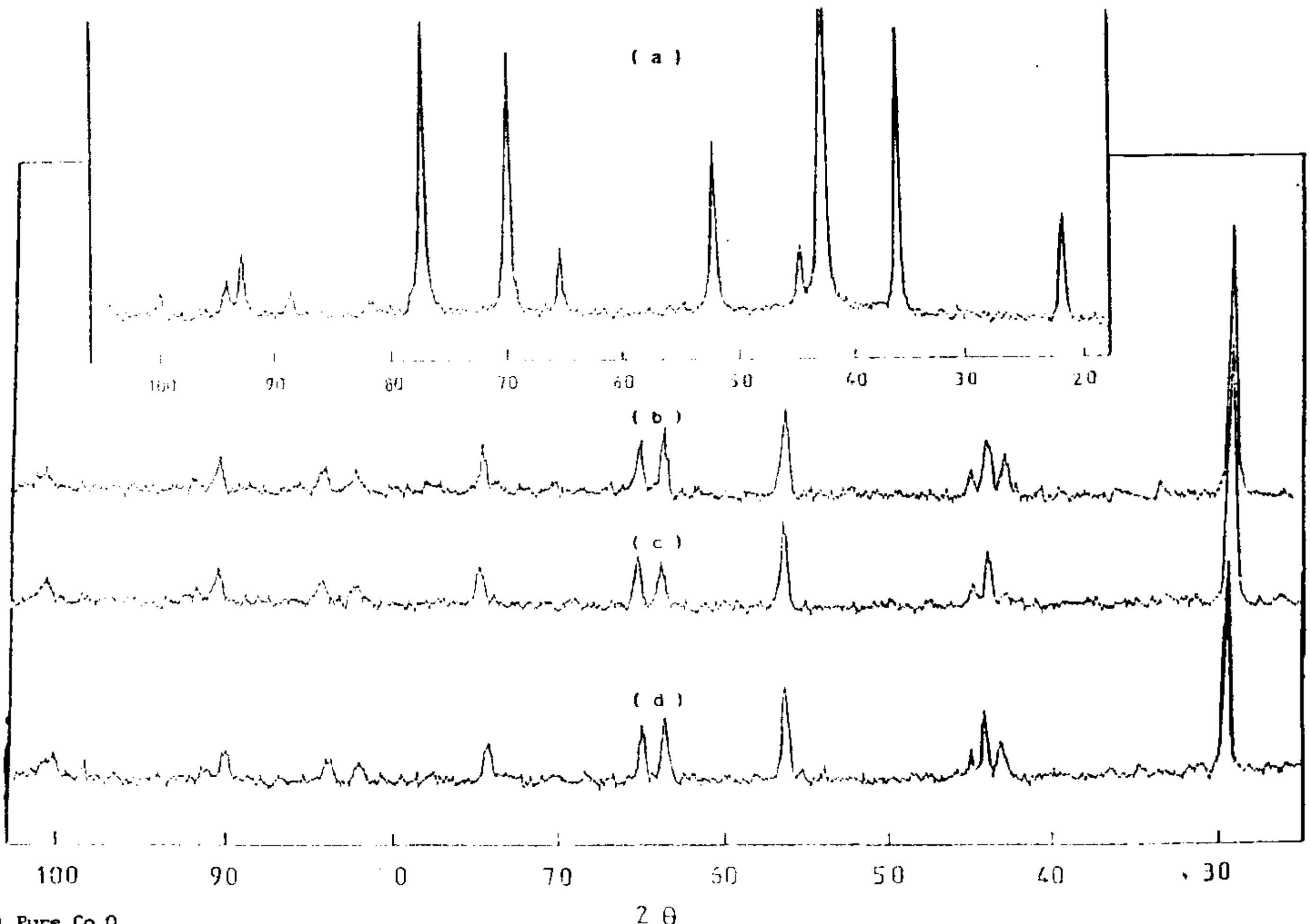
Table 2.

SOLID DESIGNATION	FRACTION OF Co_3O_4		$(a)_{extr.}$ m.mole.H_2O_2 g^{-1} Co_3O_4
	Extracted (m.mole/ g Co_3O_4)	Interacted (m.mole/g Co_3O_4)	
Pure Co_3O_4	3.073	1.079	0.743
Pure TiO_2	----	----	----
Supported Co_3O_4/TiO_2 (CT)	3.778	0.374	0.743
V_2O_5 doped Co_3O_4/TiO_2 (CTV I)	3.272	0.883	1.006
V_2O_5 doped Co_3O_4/TiO_2 (CVT II)	3.799	0.353	0.818

Dissolution and specific activity $(a)_{extr}$ of catalyst sample



XRD patterns of

(a) Pure Co_3O_4

(b) Pure TiO_2

(c) Supported Co_3O_4 / TiO_2

(d) V O doped Co O / TiO

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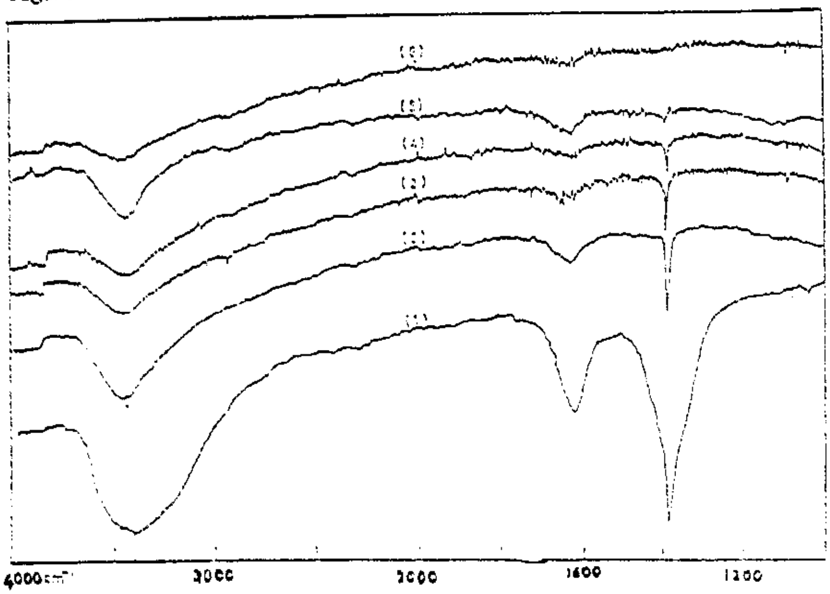
Figure 2.



R absorption spectra of :

(1) Cobalt nitrate

(2) Catalyst sample prepared by decomposing Cobalt nitrate at 110°C

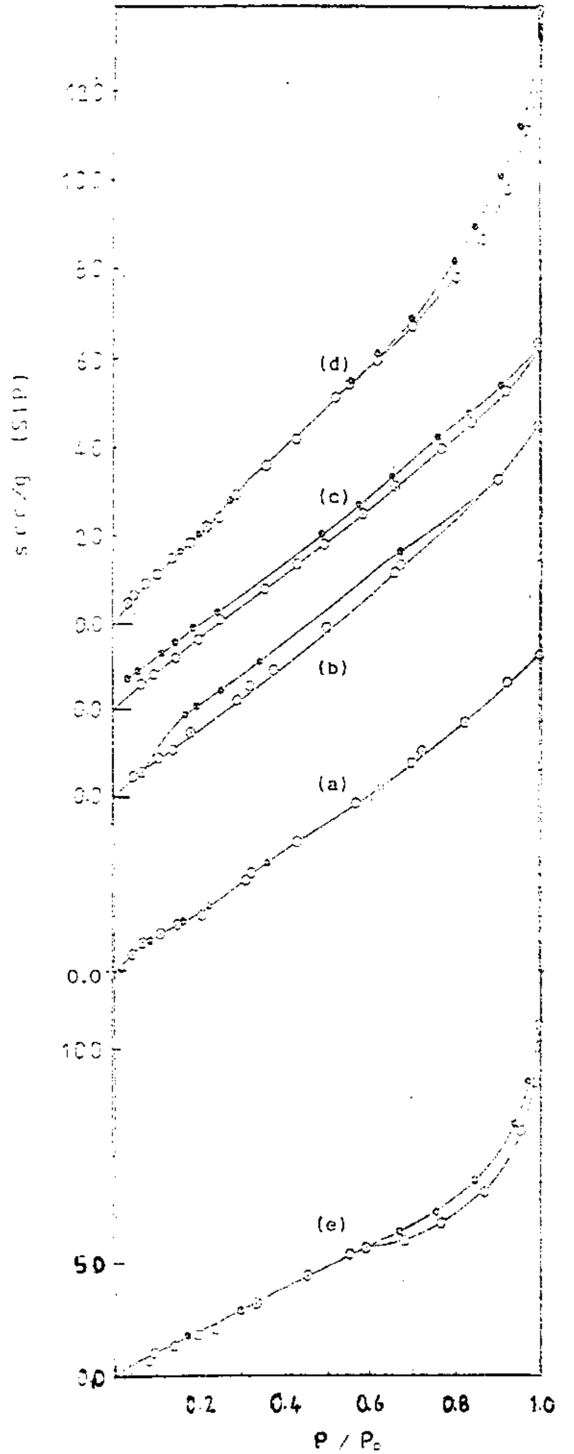
(3) Catalyst sample prepared at 150°C

(4) Catalyst sample prepared at 190°C

(5) Freshly prepared Co_3O_4/TiO_2

(6) Co_3O_4/TiO_2 thermally treated at 400°C

Figure 3.



Low temperature adsorption-desorption isotherms of N_2 on :

(a) Pure TiO_2

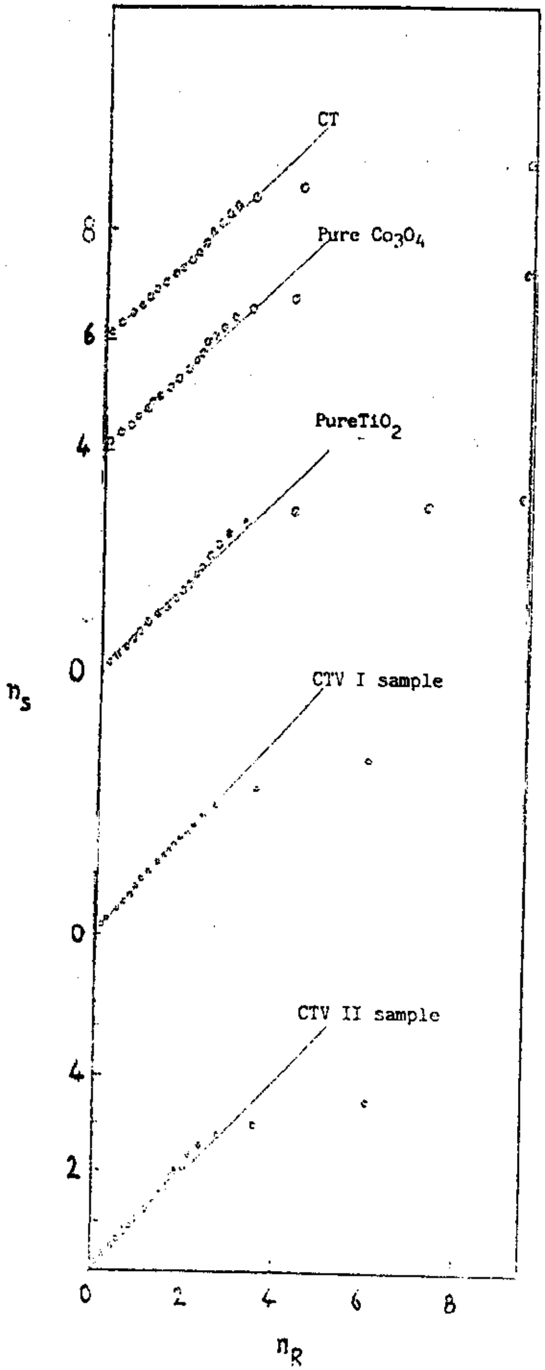
(b) Pure Co_3O_4

(c) Co_3O_4 / TiO_2

(d) CTV I sample

(d) CTV II sample

Figure 4.



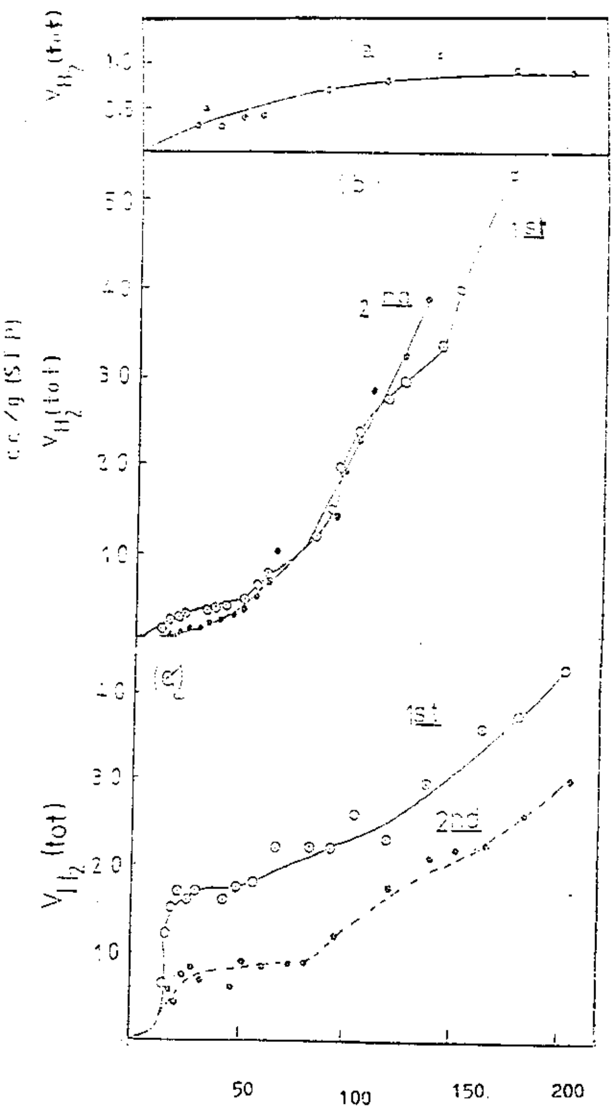
n_S - n_R plots for :

(a) Pure TiO_2 (b) Pure Co_3O_4

(c) CT sample (d) CTV I sample

(e) CTV II sample

Figure 5.



Total uptake of H_2 at 330°C for :

(a) Pure TiO_2

(b) Pure Co_3O_4

(c) CT catalyst sample

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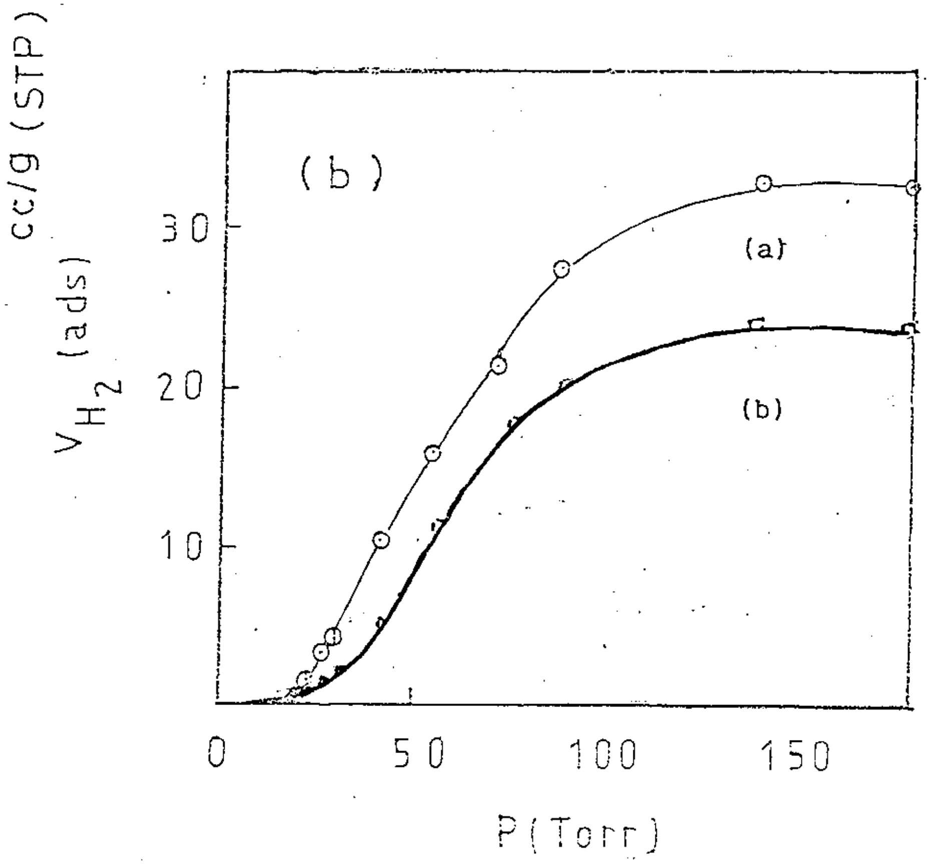
Figure 6.



H_2 - adsorption isotherms on :

(a) CTV I

8b) CTV II

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تأثير طريقة الإشابة بخامس أكسيد الفاناديوم على خصائص أكسيد التيتانيوم الحفاز المحمل بأكسيد الكوبالت

صلاح عبده حسن - محمد أحمد مكيوى - سلوى أحمد صادق

قسم الكيمياء - كلية العلوم - جامعة عين شمس - العباسية - القاهرة ٠

في هذا البحث تم دراسة خواص أكسيد التيتانيوم الحفاز المحمل بأكسيد الكوبالت والمشوب بخامس أكسيد الفانديوم لبيان تأثير طريقة الإشابة ٠

فقد وجد أنه إذا تمت الإشابة بطريقة التغطية السطحية فإن كيمياء رابع أكسيد الكوبالت النشط قد تغيرت بشكل ملحوظ منعكسة بذلك على خواصه السطحية ونشاطه النوعى وكذا إنخفاض ملحوظ فى النوعيات المستخلصة والإدمصاص الكيميائى للهيدروجين ٠ فى حين أن الإشابة بطريقة الإنتشار التبادلى لم تؤدى إلى تغير يذكر فى خصائص الحفاز الأصلى ألا وهو أكسيد التيتانيوم المحمل بأكسيد الكوبالت ومع ذلك فقد تم تحديد بعض الإختلافات فى النشاط النوعى ٠