

Notes

Surface properties and catalytic activity of vanadia supported on samaria

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Sm₂O₃ - vanadia catalysts have been prepared by wet impregnation method using NH₄VO₃ solution. The surface properties of the prepared catalysts have been studied using FTIR, XRD, surface area and pore volume data. The acid-base properties of the system have been investigated by titrimetric method using Hammett indicators, adsorption of electron acceptors as well as decomposition of cyclohexanol. Phenol alkylation reaction by methanol has been carried out to investigate the catalytic activity. It has been observed that the selectivity of the products depends upon the composition of the supported system.

Supported metal oxides exhibit interesting catalytic behaviour depending on the kind of support, the content of active component and the preparation method. In particular, vanadium oxide catalysts in combination with various promoters are widely used for several reactions including oxidation of hydrocarbons^{1,2}, ammoxidation of aromatics and methyl aromatics³ and selective catalytic reduction of NO_x by ammonia⁴. Supported vanadia catalysts possess a molecularly dispersed V-oxide, which is more active than bulk V₂O₅. Supports are used to improve thermal stability, mechanical strength and life time of the active species⁵. In addition, the extent of vanadia loading, is also crucial. Depending on the extent of loading various surface species have been reported. Isolated mono oxo species and two dimensional V-oxide clusters correspond to low surface coverage whereas a separate V₂O₅ phase and polyvanadates are observed at higher coverage⁶.

Oxidative dehydrogenation of propane over Sm₂O₃-V₂O₅ system has been reported by Corma *et al.*⁷ Sm₂O₃ being a considerably basic catalyst, apart from surface vanadyl species, orthovanadates have also been detected⁷. Patel *et al.* have reported oxidative dehydrogenation of butane over samarium orthovanadate⁸. In this note we report the acid-base property of vanadia-samaria system and its correlation with the catalytic activity towards alkylation of phenol.

Alkyl phenols are very important raw materials for the synthesis of a variety of agrochemicals, pharmaceuticals and polymers⁹. The catalysts generally employed for the alkylation reaction include various types of zeolites, γ -alumina, H₃PO₄, metal phosphates, acidic and basic metal oxides, etc., which produce both O- and C-alkylated products. The selectivity of the products was found to depend upon the acid-base property of the catalysts employed^{10,11}. Selective alkylation of basic catalysts such as MgO at the *ortho* position has been reported by Tanabe *et al.*¹². Benzouhanava has claimed that strongly acidic sites favour O-alkylation to give anisole as the major product while strong basic sites and weak acid sites prefer C-alkylated products¹³. However, a contradictory claim has been put forward by Rao *et al.* that strongly acidic sites promote ring alkylation⁹. The aim of the present investigation is to understand the selectivity and activity of vanadia-samaria systems for the methylation of phenol.

Experimental

Samaria was obtained by precipitation via hydroxide method from its nitrate solution. The supported catalyst was prepared by wet impregnation method as reported earlier by stirring an aqueous oxalic acid solution of NH₄VO₃ with Sm₂O₃ followed by evaporation and calcination at 723 K for 6 h. The following compositions of V₂O₅ were selected in the present study, namely 3, 7, 11 and 15 wt % of vanadia which are denoted as S3, S7, S11 and S15 respectively. The calcined samples were powdered below 100 mesh size and activated at 773 K for 2 h prior to each experiment.

For phase identification, powder XRD patterns were obtained using a Ni filtered Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$). Micromeritics Flowprep -060 instrument was used to determine the surface area by nitrogen adsorption. FTIR spectra of samples were measured by KBr disk method. Measurement of pore volume and pore size distribution of the catalysts were carried out using Quantachrome, Auto scan-92 porosimetry (USA).

Hammett indicator method as well as adsorption of electron acceptors was used as a measure of basicity. The following indicators were tried for basicity determination (*pK_a* values are given in parenthesis).

Crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). Of these, the catalysts responded only to dimethyl yellow, methyl red and bromothymol blue. In the indicator method, two drops of 0.1% solution of indicator in benzene were added to a suspension of the catalyst in benzene and titrated against trichloroacetic acid until a permanent colour change was obtained. Adsorption of electron acceptors was investigated to study and characterise the electron donating property of the system. The following electron acceptors were used in the present study (electron affinity in eV given in parenthesis): 7,7,8,8-tetracyanoquinodimethane (TCNQ) (2.84), chloranil (2.40), *p*-dinitrobenzene (PDNB) (1.77) and *m*-dinitrobenzene (MDNB) (1.26). Experimental procedure for adsorption studies is reported elsewhere¹⁴. The amount of electron acceptor adsorbed on the catalyst surface was estimated by measuring the absorbance at the λ_{\max} of the electron acceptor (EA) with a Shimadzu 160-A spectrometer. The λ_{\max} of TCNQ and chloranil in acetonitrile are 393.5 nm and 288 nm respectively. Adsorption of PDNB and MDNB was so negligible that they could not be measured. Isotherms obtained were of Langmuir type. From the Langmuir adsorption isotherms, limiting amount of electron acceptor adsorbed was calculated.

For comparing acidity, cyclohexanol decomposition was used as a test reaction. Catalytic activity was determined by phenol alkylation reaction. The reactions were carried out in a flow type gas phase reactor kept in a cylindrical furnace mounted vertically. Catalyst (3 g) was loaded in the middle of the reactor packed with glass beads. The catalysts were activated in a current of dry air prior to each experiment. The products were analysed by means of a gas chromatograph (GC 15-A) fitted with a SE30 column using FID.

Results and discussion

The physicochemical characteristics of the catalysts are presented in Table 1. Samarium orthovanadate (SmVO_4) was also detected in the XRD data along with samarium oxide as reported by Corma *et al.*⁷ (Fig. 1). The ratio of intensities of the characteristic peaks orthovanadate/samaria increases when Sm/V atomic ratio decreases. From the XRD data it was found that crystalline V_2O_5 is not there in the supported catalysts even at higher wt% of vanadia. FTIR data of these systems confirms this inference

(Fig. 2). The characteristic band of V_2O_5 is not observed in the spectrum at 1020 cm^{-1} . The weak band $\sim 1060\text{ cm}^{-1}$ is attributed to V=O stretching mode that arises from surface vanadyl species. The fact that only one frequency of V=O vibration is observed leads to the absence of O=V=O fragments on the surface species. High value of V=O stretching frequency indicates the absence of poly vanadyl surface species. As shown by Frederickson and Hausen, crystalline polyvanadates manifest V=O stretching frequencies in the $1000\text{-}950\text{ cm}^{-1}$ region¹⁵.

Table 1—Physico-chemical characteristics of $\text{V}_2\text{O}_5\text{-Sm}_2\text{O}_3$ catalysts

| Catalyst | BET surface area(m^2/g) | Pore volume (cm^3/g) | Limiting amount of EA adsorbed ($10^6\text{ mmol}/\text{m}^2$) | |
|-------------------------|---|--|--|-----------|
| | | | TCNQ | Chloranil |
| Sm_2O_3 | 20.79 | 1.41 | 3.05 | 2.93 |
| S3 | 17.19 | 0.89 | 5.27 | 4.38 |
| S7 | 21.90 | 0.64 | 4.30 | 3.53 |
| S11 | 25.54 | 0.67 | 2.29 | 1.90 |
| S15 | 23.47 | 0.59 | 2.26 | 1.27 |

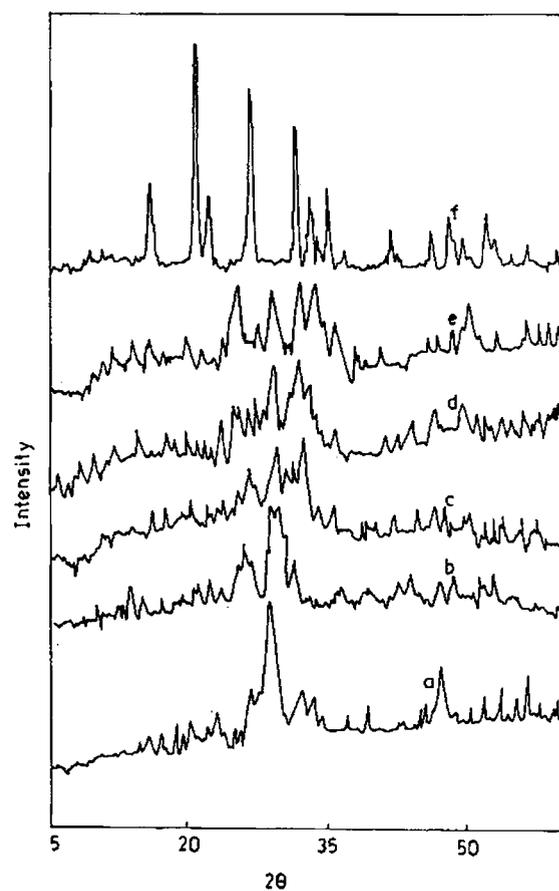


Fig. 1—XRD patterns of vanadia supported samaria. [a, Sm_2O_3 ; b, 3% V_2O_5 ; c, 7% V_2O_5 ; d, 11% V_2O_5 ; e, 15% V_2O_5 ; f, V_2O_5].

One broad band is observed in the range 700-900 cm^{-1} which accounts for the VO_4^{3-} entity that results from orthovanadate¹⁶. The intensity of the bands in the hydroxyl region is decreased for supported system indicating the participation of surface hydroxyls in bond formation with vanadia. Besides, there is a shift of the band to lower frequency. The IR band at higher frequency has been assigned to the most basic hydroxyl group. The surface metal oxide species coordinate to the oxide support by titrating the basic surface hydroxyls of the support.

Basicity measurements adopting Hammett indicators show that acid-base property of the system

Table 2—Basicity of vanadia supported on samaria

| Catalyst | Basicity (mmol/g) | | |
|-------------------------|-------------------|-----------------|-----------------|
| | $pK_a \geq 3.3$ | $pK_a \geq 4.8$ | $pK_a \geq 7.2$ |
| Sm_2O_3 | 0.346 | 0.084 | 0.059 |
| S3 | 0.279 | 0.072 | 0.047 |
| S7 | 0.180 | 0.065 | 0.051 |
| S11 | 0.147 | 0.063 | 0.048 |
| S15 | 0.116 | 0.055 | 0.042 |

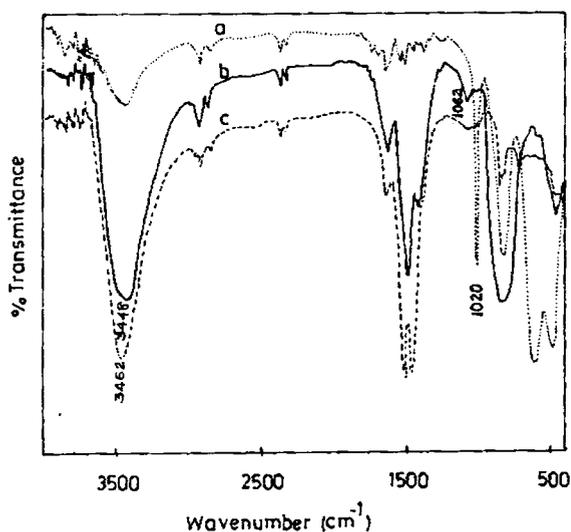


Fig. 2—FTIR spectra of Sm_2O_3 and $\text{V}_2\text{O}_5/\text{Sm}_2\text{O}_3$ along with pure V_2O_5 [a, V_2O_5 ; b, S 15; c, Sm_2O_3]

is greatly influenced by the addition of V_2O_5 (Table 2). Basicity decreased as the composition of vanadia was increased from 3-15 wt%. Brönsted acidity has also been measured by Hammett indicator method¹⁷. So, the decrease in basicity may be due to removal of basic surface OH groups during impregnation by the bond formation with vanadia salt which agrees with the IR data. This observation is supported by the data from electron donating property of the system. Electron donor strength of a surface is defined as the conversion power of the electron acceptor adsorbed to its anion radical. The extent of electron transfer decreases with decrease in electron affinity value of the electron acceptor. If the electron acceptor is strong, anion radical formation occurs both at strong and weak donor sites. But if it is weak, adsorption occurs only at stronger sites. From the Table it is clear that limiting amount of electron acceptor adsorbed decreases in the order $\text{S3} > \text{S7} > \text{S11} > \text{S15}$.

The amphoteric character of the alcohols permits their interaction with acidic and basic sites. Dehydrogenation takes place with the intervention of both acidic and basic sites and dehydration takes place with the participation of acidic sites. Hence, dehydrogenation rate is proportional to both acidity and basicity whereas dehydration is found to be proportional to acidity alone, which means that dehydration activity or selectivity for dehydration products can be taken as a measure of the acidity of the system.

Cyclohexanol decomposition is usually studied to check the acid-base property of the system. For pure samaria, dehydration is prominent which leads to cyclohexanone in major amounts indicating strong basic sites on the catalyst. For supported vanadia systems, dehydration products predominate. From Table 3, it is clear that as the content of vanadia in the system is increased, the selectivity of dehydration products shows a corresponding increase; the order being $\text{S3} < \text{S7} < \text{S11} < \text{S15}$. According to

Table 3—Decomposition of cyclohexanol over the different catalysts [Reaction conditions: catalyst = 2.5 g; reaction temp. = 623 K; feed rate = 6 ml/h, TOS = 1 h].

| Catalyst | Conversion (%) | Product distribution (%) | | | Selectivity (%) | |
|-------------------------|----------------|--------------------------|-------------|---------------|-----------------|-------|
| | | MCP | Cyclohexene | Cyclohexanone | C=C | C=O |
| Sm_2O_3 | 40.85 | - | 10.95 | 29.90 | 26.81 | 73.19 |
| S3 | 38.61 | 1.19 | 33.73 | 3.69 | 90.44 | 9.56 |
| S7 | 39.59 | 2.12 | 34.09 | 3.38 | 91.46 | 8.54 |
| S11 | 42.40 | 3.43 | 35.76 | 3.21 | 92.42 | 7.58 |
| S15 | 43.07 | 3.63 | 36.34 | 3.10 | 92.80 | 7.20 |

Table 4—Selectivity of products in the methylation of phenol over supported vanadia catalysts [Reaction conditions: catalyst = 3 g; reaction temp. = 623 K; Phenol : methanol ratio = 1 : 7; Feed rate = 4 ml /h. TOS = 1.5 h].

| Products | Catalyst | | | | |
|------------------|----------|-------|-------|-------|-------|
| | S | S3 | S7 | S11 | S15 |
| Anisole | 5.69 | 3.53 | 3.20 | 5.48 | 4.41 |
| Methyl anisole | 3.16 | - | - | 10.56 | 9.33 |
| <i>o</i> -Cresol | 38.38 | 65.73 | 47.94 | 31.66 | 22.33 |
| 2,6-Xylenol | 20.88 | 26.85 | 37.35 | 23.54 | 26.05 |
| TMP | 1.89 | 3.89 | 11.51 | 28.76 | 37.88 |

Benzouhanava *et al.*, Brønsted acid sites catalyse dehydration¹⁸. So vanadia incorporation is expected to enhance the Brønsted acidity. Brønsted acidity in the case of supported catalysts is located at support – O – V bonds, even though no spectroscopic evidence exists in favour of this¹⁹. Enhancement of Brønsted acidity by such a vanadate layer is exhibited by alumina supported vanadia²⁰. Increase of Brønsted acidity by vanadia addition is also reported by Hatayama and co-workers²¹. Considerable amount of methyl cyclopentene (MCP) is also formed by the isomerisation of cyclohexene. This indicates that the generation of stronger acid sites on the catalyst surface as the vanadia loading is increased as suggested by Pines *et al.*²². However, the conversion of cyclohexanol does not vary much even after adding 15% of vanadia to Sm₂O₃. This can be accounted for by their surface areas. The surface areas do not show a marked variation. The trend in the surface areas almost matches with the activity towards decomposition.

Phenol alkylation data is presented in Table 4. From the data it is clear that C-alkylation is predominant over these catalyst systems. This is in accordance with the observation of Benzouhanava *et al.* that weak acid sites and/or strong basic sites favour C-alkylated products rather than O-alkylated products. Maximum *ortho* selectivity (*o*-cresol and 2,6-xylenol) is achieved in the case of S3 due to high basicity as compared to other compositions. Since strong acid sites are absent, the phenolate anion is adsorbed in such a way that *ortho* positions are near the surface leading to *ortho* methylation. As the vanadia composition in Sm₂O₃ is increased, trimethyl phenol selectivity increases which can be attributed to decrease of basicity. This increase of trimethyl phenol selectivity correlates well with the acidity as evidenced from the cyclohexene selectivity.

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