

Synthesis, characterisation and benzylation activity of vanadia impregnated iron pillared montmorillonite

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Iron pillared montmorillonite has been synthesised and it is then wet impregnated with vanadia with different vanadia composition. These catalysts are characterised using conventional techniques such as XRD analysis, FTIR analysis, and surface area and pore volume measurements. Acidity is measured using spectrophotometric monitoring of adsorption of perylene, thermogravimetric desorption of 2,6 dimethylpyridine and temperature programmed desorption of ammonia. Activity studies are done in the liquid phase. It has been concluded that Lewis acidic sites are responsible for the benzylation of toluene when the benzylating agent is benzyl chloride while Brønsted acidic sites are responsible when the reagent is benzyl alcohol.

Supported vanadium oxide catalysts are important in industrial processes¹⁻³. Use of supporting vanadium oxide on another oxide has several advantages over an unsupported oxide, such as higher mechanical strength, better thermal stability and larger surface area⁴. There are several reports regarding the dispersion of vanadium oxide over basic, amphoteric and acidic oxides⁵⁻⁷. It is possible that the dispersion of vanadium oxide as well as the structure can be understood on the basis of acid-base character of the supports used. The basic and amphoteric oxides favour the bidimensional dispersion, often with the formation of vanadates. The agglomeration of vanadia species to form crystalline vanadia is favoured with the acid character of the support. Except a few reports^{8,9}, work on vanadia impregnation over clays is very rare. Over acid activated montmorillonite, K10, vanadia loading by wet impregnation method was attempted and compared with vanadia-silica by Narayanan and coworkers⁸. They have inferred that the type of interaction of vanadia with K10 montmorillonite is different from that with silica. Vanadia is well dispersed as V₂O₅ crystallites in both the supports. An interaction of vanadia with the support occurs in the case of silica whereas such interaction is absent in montmorillonite K10. An interaction between vanadia and the support leads to the hyperfine splitting of ESR spectra, and is observed with the case of silica but not with K10 montmorillonite. In our present investigation, we have prepared iron-pillared clay and various vanadia

loaded iron-pillared clays by the wet impregnation method. All the samples were characterised employing the techniques such as EDX, XRD, FT-IR, surface area and pore volume measurements and acidity determination studies by perylene adsorption technique, thermogravimetric desorption of 2,6-dimethylpyridine (DMPY) and temperature programmed desorption (TPD) of ammonia. These solids were tested for activity in the Friedel-Crafts benzylation of toluene. Friedel-Crafts alkylation reactions are very important from synthetic and industrial points of view. These are important means for attaching alkyl chains to aromatic rings. On behalf of the strict environmental regulations and drive towards clean technology, the present tendency is to replace the conventional technology using homogeneous catalysts by environmentally friendly catalysis, typically involving the use of solid acid catalysts¹⁰.

Materials and Methods

Preparation of iron-pillared and vanadia loaded iron-pillared montmorillonites

The starting material used for the work is KSF montmorillonite obtained from Fluka. This material has a chemical composition (wt %) of Si-59.57%, Al-21.05%, Fe-10.73%, Ca-3.48%, K-1.86%, Mg-2.32% and Na-0.97% and a surface area of 6.6 m²g⁻¹. Iron-pillared montmorillonite (FePM) was prepared by stirring a 1% suspension of the parent montmorillonite in distilled water added to the

pillaring solution which is previously prepared by partially hydrolysing 0.2 M ferric nitrate solution with 0.3 M sodium carbonate at a base/metal ratio of 2.0 under vigorous stirring at 70°C for two hours followed by continuous stirring for six hours at room temperature. Fe³⁺ to clay ratio was maintained as 20 mmol g⁻¹ of clay in the final reaction mixture. After reaction, the material was washed until flocculation appeared and it became nitrate free. It was then dried at 110°C, followed by controlled calcination in dry air at 400°C for five hours to get iron-pillared montmorillonite catalyst. Different percentages of vanadia were loaded over FePM according to the wet impregnation method¹¹. Calculated amounts of ammonium metavanadate corresponding to 2, 5, 7, 10, 15 and 20 weight percentages of vanadia were dissolved in aqueous oxalic acid solution and stirred with iron pillared montmorillonite for 3 hours followed by solvent evaporation on a water bath. These were then oven-dried overnight and calcined at 400°C for five hours. The samples are denoted as XVFe, where X represents the percentage of vanadia loaded over FePM.

The percentage of vanadia was determined by EDX spectroscopy performed over an EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si-Li detector, sensitivity > 0.1 wt%). The XRD patterns of the prepared samples were recorded using Rigaku Model D/Max C instrument. FTIR spectra of the powdered samples were measured by the KBr disk method over the range 4000-400 cm⁻¹. Shimadzu DR 8001 instrument was used for the purpose. The surface area of the catalysts was determined by BET nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Flow Prep 060 instrument. Previously activated samples were preheated and degassed at 473 K for two hours under nitrogen flow. The catalyst was then brought to 77 K using liquid nitrogen for adsorbing nitrogen gas at various pressures. The total pore volumes of the samples were also measured using the same instrument. This was measured by the uptake of nitrogen at a relative pressure of 0.9. Acidity was determined by three independent methods: (i) Thermogravimetric desorption of DMPY-Previously activated catalysts were kept in a desiccator saturated with vapours of DMPY at room temperature for 48 hours. Then the catalysts were subjected to thermogravimetric analysis when the weight loss of the adsorbed sample was monitored for the range 40-500°C at a rate of 20°C/min. The fraction of weight loss in the range 250-500°C was

found out and taken as a measure of the Brønsted acidity of the samples¹²⁻¹⁵. (ii) Perylene adsorption studies-Different concentrations of perylene in benzene were prepared and stirred with about 0.5 g of the activated catalyst at room temperature for four hours. Due to adsorption of perylene on the catalyst from the solution, its concentration in the solution will be less after adsorption. The difference in concentration before and after adsorption was determined by means of a Shimadzu UV-VIS spectrophotometer. The absorbance was measured at a λ_{\max} of 439 nm. (iii) Temperature programmed desorption of ammonia-About 0.75 g of the previously activated catalyst was degassed by heating in a stream of nitrogen at 300°C. It was then cooled to room temperature. The ammonia was allowed to be adsorbed on the catalyst by injecting 15 mL of ammonia gas at room temperature into a stainless steel reactor of 30 cm length and 1 cm diameter in which the catalyst was kept. The catalyst was then heated through a temperature programme in nitrogen flow. At each interval of 100°C, the ammonia desorbed was trapped using nitrogen as the carrier gas in a stoppered conical flask containing a known excess of 0.025 N sulphuric acid for the temperature range 100-600°C. It is estimated by the back titration of the excess sulphuric acid using standard NaOH. The amount of ammonia desorbed was distributed in the weak plus medium strong (100-400°C) and strong acid regions (400-600°C).

Activity studies

Friedel-Crafts alkylation of toluene with two different benzylating agents such as benzyl chloride and benzyl alcohol was carried out in the liquid phase in a 50 mL R.B. flask equipped with an oil bath, a magnetic stirrer and a water condenser. The reaction mixture was analysed at required time intervals using a Chemito GC-8610 equipped with an SE 30 column and flame ionization detector.

Results and Discussion

Methods of characterisation-XRD and IR studies

Table 1 shows the XRD details of FePM and all the vanadia impregnated iron pillared systems along with those of pure V₂O₅. The characteristic 2 θ value of the original montmorillonite (corresponding to a layer distance of 9.82Å) is shifted from 9 to 5.72 and the layer distance is correspondingly increased to 15.48Å for FePM. The other peaks at 19.2 and 25.7 are due to

Catalyst	2 θ	<i>d</i> spacing	Relative Intensity
FePM	5.72	15.48	69.21
	19.7	4.51	100
	25.2	3.55	30.10
2VFe	5.71	15.50	51.50
	19.8	4.49	100
	25.1	3.55	27.89
5VFe	5.72	15.48	38.10
	19.75	4.50	100
	25.1	3.55	26.24
7VFe	5.71	15.50	26.41
	19.66	4.52	100
	25.15	3.54	28.01
10VFe	19.66	4.52	100
	25.15	3.54	17.81
	26.10	3.41	26.10
	32.05	2.79	24.10
	35.65	2.51	28.10
15VFe	54.01	1.69	24.01
	19.91	4.46	100
	25.48	3.50	16.10
	26.18	3.40	28.09
	32.14	2.78	24.51
20VFe	35.15	2.55	31.01
	54.08	1.69	22.08
	19.76	4.51	100
	25.15	3.54	19.62
	26.04	3.41	31.04
V ₂ O ₅	32.28	2.77	27.91
	35.65	2.51	44.41
	55.01	1.66	28.04
	20.05	4.43	100
	26.20	3.40	63.87
	32.45	2.76	29.31
	34.45	2.6	45.22
	55.75	1.64	15.52

the quartz impurity. It is well-known that loading of vanadia over basic oxides results in compound formation such as orthovanadate or pyrovanadate formation^{5,6}. But with acidic oxides, no such compound formation is expected. Instead, V₂O₅ aggregates dispersed over the solid surface are observed⁷. Clays, especially pillared clays are well-known as acidic oxides. Hence dispersion of V₂O₅ over the solid surface is expected. From Table 1, it is clear that the addition of vanadia up to 7 wt% on iron-pillared montmorillonite, did not show any characteristic peak of pure V₂O₅. However, with the increased loading of vanadia such as 10 wt% and above, peaks characteristic of vanadia start to appear. The intensity of the vanadia peak increases with the vanadia content and the peak corresponding to the

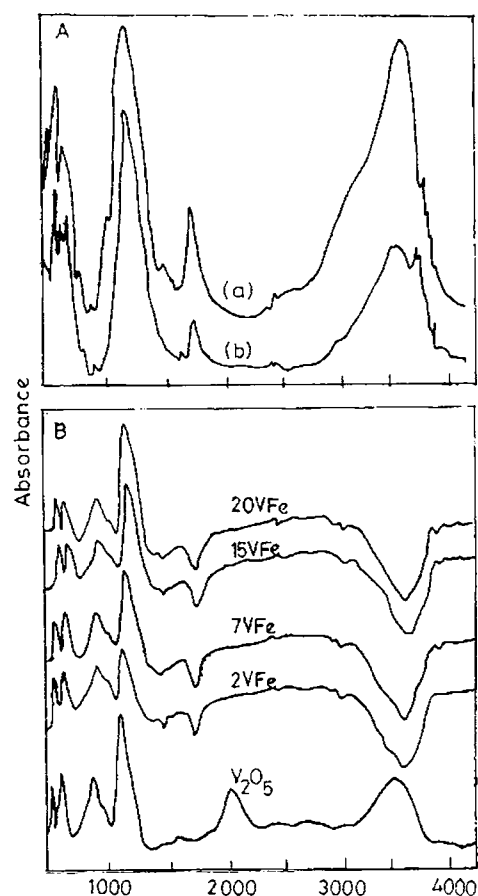


Fig 1—A. IR spectra of (a) parent montmorillonites and (b) FePM. B. IR spectra of vanadia loaded iron pillared montmorillonites after subtracting that of FePM

expansion of layers during pillaring in FePM, becomes weak and it is almost disappeared when the vanadia loading reaches 10 wt%. These facts suggest the distribution of vanadia on the pillared montmorillonite as small crystallites. However, these are not detectable by XRD technique when the vanadia content is 7% or below. The crystallite size of vanadia seems to increase with vanadia loading beyond 7% and becomes detectable by XRD. Comparison between the IR spectra of parent montmorillonite and the pillared samples reveals that the basic structure of clay is not at all altered during the pillaring process since all the main peaks are retained in the pillared samples (Fig. 1 A). IR results are also examined to find out the nature of vanadia species over FePM. Figure 1 B shows the IR spectra of FePM and the IR spectra of XVFe_s after subtracting the IR of FePM. This subtraction is done in order to nullify the sharp peak due to Si-O bond that may overlap on the peak due to vanadia and this enables to find out the modification caused by

Table 2—Vanadia percentage, surface area and pore volumes of vanadia impregnated iron-pillared montmorillonites

Catalyst	Vanadia content (wt %)	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
FePM	0.00	188.7	0.1435
2VFe	2.01	124.9	0.1040
5VFe	4.98	94.0	0.1017
7VFe	7.40	72.4	0.0732
10VFe	10.55	36.6	0.0378
15VFe	15.02	26.0	0.0344
20VFe	20.04	14.6	0.0210

vanadia impregnation alone. The characteristic mode of V_2O_5 at 1020 cm^{-1} ($\text{V}=\text{O}$ stretching) is shown by all the vanadia impregnated FePMs¹⁶. As the percentage of vanadia increases, the intensity of this peak also increases. Thus the distribution of V_2O_5 over FePM is further confirmed by the IR results.

Table 2 presents the vanadia composition, surface area and pore volume of the various systems. The pillaring of montmorillonite causes a dramatic increase of surface area from 6.6 to $188.67\text{ m}^2\text{g}^{-1}$. But the incorporation of vanadia results in the continuous decrease of surface area and also pore volume. We have already seen the formation of V_2O_5 on FePM while treating it with ammonium metavanadate by analysing the XRD and IR results. The decrease in surface area and pore volume suggests the intrusion of vanadia species on the pores of FePM. As the percentage of vanadia loading increases, the surface area and pore volume decrease due to the greater intrusion of vanadia inside the pores. The surface area of 20VFe is dramatically reduced to $14.63\text{ m}^2\text{g}^{-1}$, which suggests almost complete blocking of the pores by the vanadia species. Similar results were obtained by Narayanan *et al.*¹⁷. The broadening of the peak corresponding to the pillaring in FePM in the XRD pattern also supports the entrance of V_2O_5 inside the pores of the pillared clay. However, the possibility of dispersal of V_2O_5 over the clay surface cannot also be ruled out.

Acidity studies

Lewis acidity by perylene adsorption method—Perylene being an electron donor transfers electron to the Lewis acid sites and gets itself adsorbed as perylene radical cation¹⁸. Thus after adsorption, the concentration of perylene in the solution decreased. This decrease was found out using absorbance measurements at λ_{max} equal to 439 nm, which corresponds to the amount of perylene getting

adsorbed on the surface, which in turn corresponds to the Lewis acidity of the system. As the concentration of perylene used for adsorption is increased, the amount of perylene getting adsorbed on the solid surface is also increased. But after a particular concentration of perylene in benzene, the amount of perylene adsorbed remains constant. This constant value is referred to as limiting amount. The limiting amount of perylene indicates the surface electron accepting capacity i.e., the Lewis acidity of the samples. Table 3 describes the Lewis acidity of the samples obtained by perylene adsorption method. Vanadia is a very weak acid and exhibits mainly Brönsted acidity^{19,21}. From the IR and XRD studies we have concluded that vanadia is dispersed as V_2O_5 inside the pores and surface of the clay lattice. Now, during the perylene adsorption experiments, we observed a significant loss of Lewis sites. It can be confirmed that loading of vanadia and thereby dispersion of vanadia as V_2O_5 did not enhance the Lewis acidity of iron pillared systems. Not only that, addition of vanadia significantly reduces perylene adsorption, due to the blocking of surface acidic sites by vanadia species.

At low vanadium loadings of 2 and 5%, Lewis acidic sites are not very much reduced. But at higher vanadium loadings, Lewis acidity is diminished due to the coverage of catalyst surface with particles of V_2O_5 . At low vanadium loadings, Lewis acidity due to exposed Fe and Al ions is present. Lewis acidity can be assigned to unsaturated vanadium ions also, due to the adsorbed V_2O_5 on the clay surface to some extent. At high vanadium loadings, crystalline vanadia covers almost the major portions of the clay, and reduced the Lewis acidity.

Determination of Brönsted acidity by thermogravimetric desorption of 2,6-dimethylpyridine—DMPY is a useful probe molecule for the selective determination of Brönsted acid sites. Several researchers applied DMPY as a probe for Brönsted acid sites¹²⁻¹⁵. DMPY desorbed above 250°C is solely attributed to the Brönsted acid sites. The selective adsorption of DMPY on Brönsted acid sites is attributed to the steric hindrance of the methyl groups²². The thermogravimetric desorption results of DMPY on the prepared samples are reported in Table 3. Vanadia addition improved the Brönsted acidity for the loading of 5VFe, 7VFe and 10VFe. This is in agreement with the Brönsted acidic nature of V_2O_5 ¹⁹⁻²¹. As the vanadia loading increases from 2%, the amount of DMPY desorbed from the catalyst

Table 3—Acidity values of different vanadia impregnated iron pillared systems

Catalyst	Limiting amount of perylene (10^{-4} mmol g $^{-1}$)	Fraction of DMPY desorbed	Acid site distribution by NH $_3$ TPD (mmol g $^{-1}$)			Total
			Weak (100-200°C)	Medium (200-400°C)	Strong (400-600°C)	
FePM	1.2104	0.024	0.2726	0.1992	0.1163	0.5881
2VFe	1.101	0.019	0.2985	0.1610	0.1314	0.5909
5VFe	0.9088	0.039	0.4263	0.4225	0.3726	1.2214
7VFe	0.7316	0.059	0.5095	0.8006	0.6186	1.9280
10VFe	0.414	0.04	0.3887	0.2682	0.3754	1.0324
15VFe	0.3421	0.028	0.3207	0.1781	0.0534	0.5522
20VFe	0.2461	0.004	0.1810	0.1011	0.0190	0.3011

also increases, up to 7% and then it decreases. We have already seen that vanadia is well dispersed over the clay surface up to the weight percentage of 7. After that, only large crystallites of V $_2$ O $_5$ are formed over the surface. These crystallites enter into the pores and thus reduce the surface area and also pore volume. It is reported that vanadia loading creates Brönsted acidity, assigned to the V-OH species of crystalline V $_2$ O $_5$ ²³. The dispersion of V $_2$ O $_5$ increases the Brönsted acidity considerably in the case of 7VFe. However, the formation of large crystallites of V $_2$ O $_5$ reduces the Brönsted acidity of the catalyst.

Temperature programmed desorption of ammonia—The distribution of acid sites and total acidity values of the various vanadia loaded iron pillared montmorillonites are also shown in Table 3. We can see that the total acidity values increases as the vanadia percentage increases from 2 to 7 and then these acidity values start to decline. This trend may be due to the high degree of dispersion of vanadia over FePM up to 7% and the formation of large crystallites at loadings greater than 7%. The large crystallites block the acid sites of the catalyst and hence the acidity is reduced. We have already seen the increase in Brönsted acidity and decrease in Lewis acidity upon vanadia addition. Thus we can assign the increase in total acidity to the effect of increasing Brönsted acidity. For 7VFe, the total acidity measured is three times greater than that of the parent iron pillared montmorillonite. Lewis acidity is decreased as evident from the values of limiting amounts of perylene adsorbed. However, we cannot rule out the possibility of NH $_3$ molecule being adsorbed on those Lewis acid sites which perylene molecule could not. It may be suspected that the total acidity values are increased (when determined by temperature programmed desorption of NH $_3$) due to this factor also, along with enhancement of Brönsted acidity. The catalysts up to 10 wt% vanadia loading, possess

Table 4—Data of benzylolation of toluene with benzyl chloride over vanadia loaded FePM

[Reaction conditions: 0.1 g catalyst activated at 500°C, benzyl chloride: toluene molar ratio 1:10, reaction temperature 60°C and time of reaction – 30 min.]

Catalyst	Conversion (%)	Selectivity (%)	
		<i>o</i> -MDPM	<i>p</i> -MDPM
FePM	86.82	23.50	76.50
2VFe	87.81	22.10	77.90
5VFe	90.21	20.41	79.59
7VFe	92.11	21.68	78.32
10VFe	64.80	19.15	80.85
15VFe	50.10	14.10	85.90
20VFe	31.01	12.21	87.79

more acidity than the parent iron-pillared montmorillonite, whereas 15VFe and 20VFe possess lesser number of acidic sites, when determined by NH $_3$ -TPD method.

Catalytic activity studies

Benzyl chloride as the reagent—The products identified were *o*-methyldiphenylmethane and *p*-methyldiphenylmethane. The percentage conversion and selectivities of *o*-MDPM and *p*-MDPM over vanadia impregnated systems are shown in Table 4. The presence of iron in the systems makes these catalysts efficient towards benzylolation of toluene. In addition, vanadia loading increased the number of acidic sites considerably up to a vanadia loading of 7% (Table 3). This increase in acidity is reflected in their activity as well. Catalysts having a vanadia loading of 7% or below are found to be more active than FePM. These catalysts enjoy high Brönsted acidity and the total acidity is also higher than parent FePM. Others show lower activity. At higher vanadia loadings, the pores are almost blocked and this results in the large reduction in surface area and catalytic

Table 5—Benzylation of toluene with benzyl alcohol over vanadia loaded FePM

Reaction conditions: 0.1 g catalyst activated at 500°C, benzyl alcohol: toluene molar ratio 1:10, reaction temperature—110°C and time of reaction – 60 min.

Catalyst	Conversion (%)	Selectivity (%)		
		<i>o</i> -MDPM	<i>p</i> -MDPM	Dibenzyl ether
FePM	47.19	51.72	33.32	14.95
2VFe	27.84	50.11	37.58	12.31
5VFe	31.92	50.65	36.23	13.12
7VFe	50.21	54.62	34.17	11.21
10VFe	41.62	39.21	42.15	18.64
15VFe	21.11	22.62	37.10	40.28
20VFe	9.62	18.19	22.37	59.44

activity. Pore blockage leads to higher selectivity for *p*-MDPM than *o*-MDPM. However, the conversion is very low for systems with high vanadia loading such as 15 and 20%, compared to systems having low vanadia loadings.

Benzyl alcohol as the reagent—We have also carried out the Friedel-Crafts reaction using a different benzylating agent such as benzyl alcohol. It is well established that the Brönsted acid sites present in a catalyst are taking part in the reaction when the benzylating agent is benzyl alcohol^{24,25}. Apart from *o*-MDPM and *p*-MDPM, dibenzyl ether is also detected as a side product in this reaction which is formed by the self condensation of benzyl alcohol. Table 5 depicts the conversion of benzyl alcohol and the product selectivity pattern for the reaction between toluene and benzyl alcohol. Vanadia addition enhanced the Brönsted acidity of the system with 7% vanadia loading and the catalytic activity is found to be more than the other loaded systems. For high vanadia loaded systems such as 15 and 20VFe, very low conversion is observed owing to their low surface areas.

The acidity determined by TPD method and thermogravimetric desorption of DMPY revealed the regular increase in both, as the loading increases. To get an insight into the decisive part playing in both the set of reactions (toluene + benzyl chloride and toluene + benzyl alcohol) we have carried out the moisture influence for the two reactions. 0.1 g each of fresh catalyst and moisture adsorbed catalyst were put into the reaction mixture containing benzyl chloride and toluene with 1:10 molar ratio in separate R.B. flasks and the reaction was carried out at 60°C. At regular intervals a small quantity of reaction mixture was

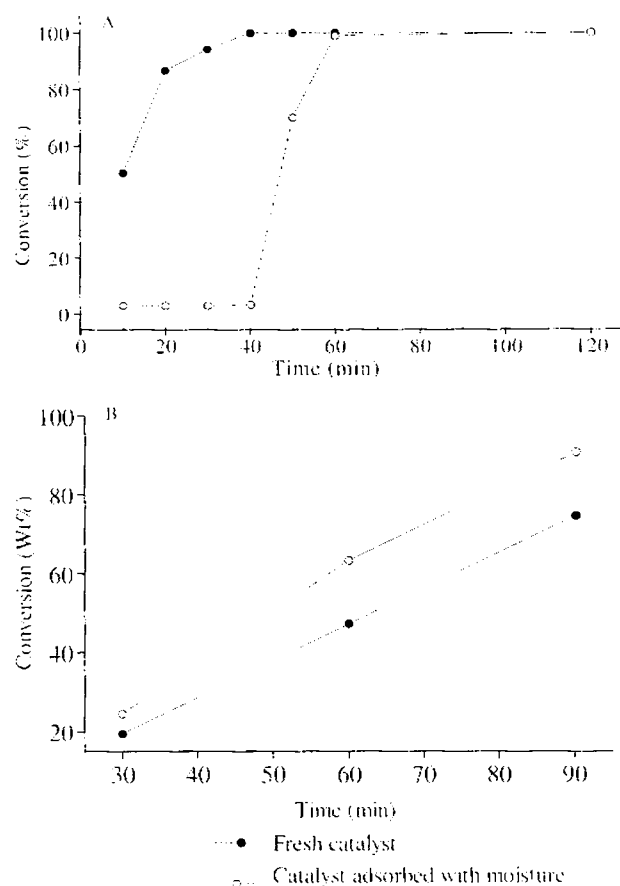


Fig. 2 — A. Conversions of benzyl chloride over fresh catalyst and catalyst adsorbed with moisture (0.1 g FePM, benzyl chloride: toluene molar ratio—1:10, reaction temperature—60°C) and B. Conversions of benzyl alcohol over fresh catalyst and catalyst adsorbed with moisture (0.1 g FePM, benzyl alcohol: toluene molar ratio—1:10 reaction temperature—110°C)

withdrawn from each of the R. B. flasks and analysed by gas chromatography. The results are illustrated in Fig. 2 A. The percentage conversion gradually increased as a function of time and became 100% at 50 minutes of the reaction, when fresh catalyst was used for reaction. But when the moisture-adsorbed catalyst was used for reaction, we have observed only negligible conversion even after forty minutes. (At this time the conversion is 94.22% for the fresh catalyst). The percentage conversion is suddenly raised from 5.29 to 69.99% in the time range 40-50 minutes. After this time, the conversion is increased steadily and became 100% after 60 minutes. Thus there is a time period for which the catalyst is inactive towards reaction, when it is adsorbed with moisture. The moisture gets adsorbed on the active sites, (Fe^{3+} and Al^{3+}) present on the interlayer and surface of the pillared clay and this prevents the benzyl chloride molecule to react over these sites. However, after the

induction period, the reaction proceeds as in the case of fresh catalyst itself.

Adsorption of moisture on the catalyst do not cause any decrease in catalytic activity when the reagent is benzyl alcohol (Fig. 2B). Instead, we noticed the catalytic activity to be higher when the moisture-adsorbed catalyst was used. When we used the catalyst after adsorbing with moisture for carrying out the reaction between benzyl chloride and toluene, we have clearly noticed an "induction period" to start the catalytic reaction. In the present case, such an induction period is not at all observed. From the results obtained, we can record that moisture has a beneficial rate enhancement effect on the reaction. The enhancement effect of catalytic activity by adsorbing the catalyst with moisture can be explained as follows. Moisture is getting adsorbed on the metal ions (Lewis acid sites) present in the catalyst and in effect, these act as Brönsted acid sites²⁶. By adsorbing on the electron deficient metal cations, the water molecules get polarised and this polarisation effect makes them efficient to carry out the reaction^{26,27}. Thus the effective number of Brönsted acid sites taking part in the reaction when the catalyst is adsorbed with moisture will be greater than those taking part in the absence of moisture. This leads to the higher percentage conversion when the reaction is carried out with a catalyst, which is adsorbed with moisture. These results indicate the involvement of Brönsted sites in the reaction.

Conclusion

Vanadia impregnation over iron pillared clay resulted in the well dispersion of V₂O₅ crystals at low vanadia loadings and agglomeration of the species at high vanadia loadings. Vanadia dispersion increased the acidity in all regions up to a particular vanadia loading, namely, 7 wt%. However, the Lewis acidity is reduced due to the blocking of active sites by vanadia species as evident from the perylene adsorption method. Moisture influence for the benzylation reaction revealed that Brönsted acidic sites are responsible for the reaction between toluene

and benzyl alcohol whereas Fe³⁺ and Al³⁺ are the active sites for the reaction between toluene and benzyl chloride. It is also concluded that vanadia addition can enhance the Friedel-Crafts reaction.

References

- Hucknal D J, *Selective oxidation of hydrocarbons* (Academic Press, London), 1974.
- Villadsen J & Livberg H, *Catal Rev Sci Eng*, 17 (1978) 203.
- Bielanski A & Haber J, *Catal Rev Sci Eng*, 19 (1979) 1.
- Villa P L in *Catalyst deactivation*, edited by B Delmon & G F Froment (Elsevier, Amsterdam), 1980, p-103.
- Blasco T, Lopez-Nieto J, Dejoz A & Vasquet M I, *J Catal*, 159 (1995) 271.
- Shon J R, Cho S G, Pae Y I & Hayashi S, *J Catal*, 159 (1996) 170.
- Lopez-Nieto J M, Kremnik G & Fiero J L G, *Appl Catal*, 61 (1990) 235.
- Narayanan S & Deshapande K, *Micropor Mater*, 11 (1997) 77.
- Narayanan S & Deshapande K, *Appl Catal A Gen*, 135 (1996) 125.
- Clark J H, Cullen S R, Barlow S J, Bastock T W, *J chem Soc Perkin Trans II*, (1994) 1117.
- Bond G C & Tahir S F, *Appl Catal*, 71 (1991) 1.
- Jacobs P A & Heylen C F, *J Catal*, 34 (1974) 267.
- Knozinger H, Kriwtenbrink H & Ratnasamy P, *J Catal*, 48 (1977) 436.
- Corma A, Rodellas C & Fornes V, *J Catal*, 88 (1984) 374.
- Miyata H & Moffat J B, *J Catal*, 62 (1980) 357.
- Reddy B M, Vijayakumar M & Jeeva Ratnam K, *Appl Catal A Gen*, 18 (1999) 77.
- Narayanan S, Deshapande K & Prasad B P, *J molec Catal*, 88 (1984) L 271.
- Kijenski J & Baiker A, *Catal Today*, 1 (1989).
- Dines T J, Rochester C H & Ward AW, *J chem Soc Farad Trans*, 87 (1991) 1611.
- Takalji M, Qwai T K, Soma M, Onoshi & Tamaru K, *J phys Chem*, 80 (1976) 430.
- Takalji M, Qwai T K, Soma M, Onoshi & Tamaru K, *J Catal*, 50 (1977) 441.
- Satsuma A, Kamiya Y, Westi Y & Hattori T, *Appl Catal A Gen*, 194 (2000) 253.
- Khader M M, *J molec Catal, A Chem*, 104 (1995) 87.
- Cseri T, Bekassy S, Figueras F & Rizner S, *J molec Catal A Chem*, 98 (1995) 101.
- Yiu H H P & Brown D R, *Catal Lett*, 56 (1998) 57.
- Arata K, Hino M & Yamagata N, *Bull chem Soc Japan*, 63 (1990) 21.
- Choudhary B M, Bhaskar V, Kantam M L, Rao K K & Raghavan K V, *Green Chemistry*, 67 (2000).