Surface acidity of V_2O_5/Al_2O_3 catalysts: IR and TPD studies

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Abstract

V_2O_5/Al_2O_3 catalysts of different vanadium contents were prepared by contacting powdered γ-Al_2O_3 with aqueous solutions of different concentrations of NH_4VO_3. Calcined catalysts with vanadium loadings below the monolayer coverage of Al_2O_3 possessed adsorbed V-oxide layer which resisted dissolution in an ammoniacal solution. On the other hand, those catalysts of higher vanadium loadings had adsorbed V-oxide layer as well as precipitated crystalline V_2O_5. The latter preferentially dissolved in NH_4OH solution. Infrared studies of chemisorbed NH_3 on V–Al-oxide catalysts as well as temperature programmed desorption (TPD) of NH_3 from these materials are reported. These studies revealed the existence of two kinds of both Lewis and Brønsted acidic sites. Below the monolayer coverage, Lewis acidity originated from Al ions uncovered with vanadia, whereas at high loadings of vanadia, this acidity is attributed to the unsaturated vanadyl groups. Regarding the Brønsted acidity, the V–OH species of the adsorbed V-oxide and the V–OH species of precipitated V_2O_5 were shown to be responsible for this acidity. TPD results showed that the NH_3 was desorbed from Lewis acid sites by heating at ≈ 440 K and from Brønsted acid sites of adsorbed V-oxide at ≈ 640 K. At higher loadings of vanadium, the Lewis acidity was diminished due to coverage with precipitated V_2O_5, whereas Brønsted acidity of these precipitates was predominant. Ammonia was desorbed from the Brønsted acidic sites of V_2O_5 particles by heating at ≈ 530 K. The various kinds of surface acidic sites were quantified by analysing the desorbed NH_3 from each kind of these sites. The present results assisted in confirming a proposed structure of the V–Al-oxide catalyst.

1. Introduction

There is a great interest in V_2O_5/Al_2O_3 catalysts because of their wide range of applications in promoting various reactions, e.g. oxidation of SO_2, CO and hydrocarbons [1–5], hydrogenation of CO and CO_2, and more recently reduction of NO by NH_3 [6–10]. As the catalytic activity of these materials is attributed, mainly, to their surface acidic properties [11–18], these characters have been the subject of several studies employing IR of NH_3 and pyridine adsorption [11,12,14,17,18]. According to these studies,

these catalysts exhibit both Lewis and Brønsted acidic characters [11,12,14–18].

It is generally accepted that the interfacial interaction between a solid substrate and a solid adsorbate as well as the extent of loading of the adsorbate greatly influence the surface structure and consequently the distribution of the various surface sites. Hence several authors have investigated the effect of these parameters on the surface structure of V–Al-oxide catalysts [2,11,17–21]. These studies suggested the formation of isolated vanadyl groups as well as two-dimensional network of vanadia species on Al_2O_3 surface at very low loadings of vanadia [2,21], whereas at higher

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loadings, the formation of complex surface polymeric compounds as well as crystallite lamellae of V_2O_5 were proposed[2,11,17,18].

To gain full identification of the surface acidic properties, few points must still be elucidated. The nature of interaction between vanadium oxide and the external surface of the carrier is to be investigated; possibly by testing the solubility of the surface vanadia in a solvent, e.g. NH_4OH. Also the influence of ways of interaction on the surface acidity may be established by IR study of chemisorbed NH_3. Moreover, a quantitative determination of the various surface sites is still necessary for complete identification of surface acidity; this can be done by applying temperature programmed desorption (TPD) of a gas with a basic character, e.g. NH_3 to the surface.

The present paper reports on the preparation of V–Al-oxide catalysts by the wet-impregnation method, and testing the solubility of these catalysts in NH_4OH solution with the objective of determining whether the interaction of vanadia with Al_2O_3 is strong via an adsorption process, or weak via a precipitation process. An IR study is also described concerning the identification of surface acidic sites by adsorbing NH_3. In addition, TPD of NH_3 is also presented aiming at determining quantitatively the various acidic sites.

2. Materials and methods

2.1. Preparation of sample

Aluminum hydroxide (Merck > 99%) was calcined in air at 773 K for 2 h to obtain γ-Al_2O_3 (surface area 183 $m^2 g^{-1}$). Ammonium metavanadate (Fluka 99%), oxalic acid (Merck 98%), vanadium pentaoxide (BDH 99.9%), ammonia (BDH 99.98%) and ammonia solution (AnalaR) were used without further purification. Aluminum oxide (1.0 g) was impregnated in aqueous solution of various concentrations of ammonium metavanadate in 100 ml, oxalic acid (1.0 M) for 30 min. at 25°C. The homogenized slurries were adjusted to 7 pH units by adding NH_4OH and

HNO_3 solution. The slurries were filtered, after centrifugation and washed several times with triple distilled water.

2.2. Analysis of dissolved vanadium

The filtrate and the washing solutions were transferred quantitatively and analysed colorimetrically for the soluble vanadium ions by the 8-hydroxyquinoline method [22]. According to this method, vanadium(V) was extracted from the aqueous solution at pH 2 by a solution of 8-hydroxyquinoline in chloroform (0.05 M) as vanadium (V) oxinate. The extract was dissolved in chloroform and analyzed colorimetrically by measuring the absorption at 550 nm.

2.3. BET surface area measurements

Each slurry was dried at 373 K (15 h), ground, calcined in flowing air at 773 K (3 h) and allowed to cool to room temperature. Multipoint BET surface area measurements were performed by using NOVA-1000 gas sorption analyzer (Quantachrome Corporation). Nitrogen was used as an adsorbate at 77 K. Naming of the samples according to the vanadium loadings as well as values of surface areas are summarized in Table 1.

2.4. The monolayer catalyst

A theoretical monolayer coverage of V_2O_5 on Al_2O_3 is predicted by considering an average V–V distance of 3.4 Å [19,21], thus a value of 4.4 V nm^{-2} (or 1.31 mmol V/g Al_2O_3) is expected for such a coverage on a 183 $m^2 g^{-1}$ Al_2O_3 surface [19,21]. The theoretical monolayer catalyst was prepared by contacting 1.0 g of Al_2O_3 to 1.31 mmol NH_4VO_3 in 100 ml of 1.0 M oxalic acid solution. This mixture was heated at 393 K to complete dryness, and was then calcined in air at 773 K (3 h).

2.5. Solubility of the adsorbed vanadium

A quantity of 1.0 g of each calcined catalyst was suspended in 100 ml 20% ammonia solution

Table 1
Adsorption of vanadium(V) from aqueous NH_4VO_3 on Al_2O_3 and its dissolution from calcined V_2O_5/Al_2O_3 catalysts into NH_4OH

Sample [a]	NH_4VO_3 (mmol) added to 1.0 g Al_2O_3	Vanadium [a] content (mmol/g Al_2O_3)	Vanadium dissolved [c] in NH_4OH solution mmol/g catalyst	BET surface area of calcined catalysts $m^2 g^{-1}$
$AV_{0.50}$	0.50	0.50	0.00	166
$AV_{0.80}$	0.80	0.80	0.00	150
$AV_{1.24}$	1.31 [b]	1.24	0.11	124
$AV_{1.13}$	1.13	1.13	0.00	128
$AV_{1.42}$	1.60	1.42	0.18	112
$AV_{4.65}$	5.00	4.65	3.22	52
$AV_{5.21}$	6.00	5.21	3.93	46

[a] Numbers refer to mmols V adsorbed on 1.0 g Al_2O_3 as calculated by quantifying the vanadium(V) concentration remaining in the filtrate and the washing solutions.
[b] mmol of NH_4VO_3 corresponding to the theoretical monolayer coverage of Al_2O_3 by V-oxide (Ref. [19,21]).
[c] 1.0 g of each calcined catalyst (773 K in air) was suspended in 100 ml 20% NH_4OH for 30 min under continuous stirring.

for 30 min with continuous stirring. The solubilities of vanadium(V) from the catalysts into the solution were determined colorimetrically by the 8-hydroxyquinoline method [22].

2.6. Chemisorption of ammonia

Chemisorption of NH_3 was established by placing the powdered catalyst in a glass boat inside a 15 cm, 14 mm i.d., glass tube reactor. The catalysts were activated by heating at 773 K (1 h) with a tubular furnace in a flow of He gas (Fluka $\approx 99\%$) previously purified by passing over oxygen trap. To prevent physisorption of NH_3, the catalysts were kept at 393 K during the experiment [14]. NH_3 was introduced into the reactor at a rate of 20 cm^3 min^{-1} for 30 min. The unadsorbed NH_3 gas was then flushed out of the reactor by flowing He at 393 K for 1 h.

2.7. IR analysis

IR spectra for Al_2O, V_2O_5 and calcined V–Al oxide catalysts were recorded on a Shimadzu FTIR 8101M infrared spectrometer. This was carried out before and after treatment with NH_3 by using self-supporting pressed discs (50 mg and 13 mm diameter). The spectral width was 4 cm^{-1} at 1000 cm^{-1}.

2.8. Temperature programmed desorption (TPD) measurements

(TPD) experiments were carried out on 200 mg of the catalyst after adsorbing NH_3 under the previous conditions. The catalyst temperature was adjusted to 323 K. A stream of He at a rate of 20 cm^3 min^{-1} was allowed to pass over the catalyst, then through a thermal conductivity detector (TCD) (Pye Unicam) which was connected to the glass reactor. The current leads of the TCD as well as those of a chromel–alumel thermocouple were connected to an X-Y recorder. The thermocouple was encapsulated inside a glass tube and placed touching the powdered samples. The thermal conductivity of the desorbed NH_3 was plotted as a function of the catalyst temperature in the range 325 to 823 K. Heating rate was linear, at 10°C/min, by controlling the input voltage to the furnace.

2.9. Quantitative determination of surface acidic sites

To quantify the desorbed NH_3 in order to determine the various acidic sites, 100 mg of the catalyst was treated in a flow of NH_3 as described before. After degasing the unadsorbed NH_3, the catalyst was heated at 503 K, then 563 and then at 723 K for 20 min in each case. The desorbed NH_3,

after each heating stage, was carried out in a stream of N_2 and trapped in a cold solution of 0.1 M HCl. NH_3 in the trap solution was analysed colorimetrically by the trichloramine method [23]. The different surface acidic sites were determined by quantifying the desorbed NH_3 at various temperatures.

3. Results and discussion

3.1. Adsorption of vanadium oxide on alumina

Table 1 lists the amount of vanadium adsorbed on 1.0 g Al_2O_3 using various concentrations of NH_4VO_3. After calcination at 773 K, the amount of vanadium (V) dissolved in an ammoniacal solution as well as the BET surface areas of the catalysts are also listed in Table 1. This table shows that when Al_2O_3 powder is suspended in NH_4VO_3 solution of concentration less than that of the theoretical monolayer coverage, (i.e. < 1.31 mmol V/g Al_2O_3), complete adsorption of vanadium on Al_2O_3 surface was established. On the other hand, at concentrations of vanadium higher than the monolayer coverage, complete adsorption of vanadium was not observed. Furthermore, catalysts of lower vanadium content were resistant to dissolution in the ammoniacal solution, whereas those catalysts of higher vanadium loading were partially dissolved in NH_4OH. These results are indications of strong interaction between vanadia and alumina at low vanadia loadings, and weaker bonding between them at high loadings.

The interaction of vanadium oxycompounds with the external surface of Al_2O_3 can either be strong via an adsorption process, or weak due to a precipitation process. The metavanadate anions in the aqueous solution of pH 7, formed polymeric species, via V–O–V bridges, whose degree of polymerization increased with the increase of the vanadium concentration [24]. Therefore, the adsorption of the polyvanadate species on Al_2O_3 surface could possibly lead, via V–O–Al bridges, to the formation of a system like that shown in
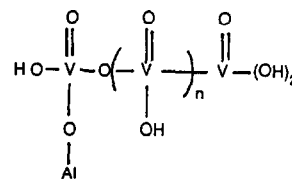
Scheme 1.

Scheme 1, where n is the degree of polymerization. According to this scheme, the vanadium surface compounds exist in the form of two dimensional network on the alumina surface [2,19,21]. These polymeric surface species existed even at a very low vanadium coverage [17,25,26], however, the possibility of forming isolated VO_4 species is not excluded [17]. Because of the relatively strong interaction of vanadium with alumina surface via V–O–Al, V–O–V and V–V bonds, these catalysts were resistant to dissolution in NH_4OH solution as indicated by the results in Table 1.

At higher loadings of vanadium, the degree of aggregation of polyvanadate anion, in the aqueous solution, was increased [24]. Further polymerization could even proceed after adsorbing the polyvanadate. This polymerization would propagate parallel and perpendicular to the alumina surface through V–O–V and/or V–V bridge, leading to the formation of a surface complex on Al_2O_3 [2,11,17,18].

In addition to the above adsorption process, at relatively high vanadium loadings, a precipitation process of vanadium oxycompounds could occur inside the pores of the carrier. Upon calcination, these precipitates could form V_2O_5 crystallites [11,17,18]. Precipitates of V_2O_5 usually form layers of $[VO_5]_n$. These layers are built up from VO_5 square pyramidal units, the assembly could hold to the alumina surface via Van der Waals interaction [21,26]. As the interaction of vanadia with alumina via the precipitation process, i.e. through the Van der Waals forces, is known to be weaker than the interaction via the previous adsorption process, one expects therefore that NH_4OH would preferentially dissolve these vanadia precipitates [17,18,27]. Moreover, during the preparation of high vanadium content cata-

Table 2
IR absorption bands, cm⁻¹, of Al_2O_3, V_2O_5 and V–Al-oxide catalysts as well as those of chemisorbed NH_3 on the same materials

| Catalyst | V=O stretching | | | Coordinately held NH₃ | | | Adsorbed NH₄⁺ on | | | | | |
| | | | | | | | OH of V-oxide adsorbed on Al₂O₃ | | | OH of V₂O₅ precipitated on Al₂O₃ | | |
	F	L	R	F	L	R	F	L	R	F	L	R
Al₂O₃	–	–	–	1235	1244, 1235, 1230	11, 14 17, 18, 29–33	–	–	–	–	–	–
V₂O₅	1023	1020	17,18	–	–	–	–	–	–	1420	1420	11,17,18,33
AV₀.₅₀	–	–	–	1235			1454	1450		–	–	–
AV₀.₈₀	–	–	–	1235	–	–	1454	1450		–	–	–
AV₁.₃₁ [a]	1023	–	–	1235	–		1450	–	–	1420	–	–
AV₄.₆₅	1025	–	–	1235	–		1450	–	–	1425	–	–
AV₅.₂₁	1025	–	–	–	–		1450	–	–	1425	–	–

F = found; L = literature; R = reference.
[a] The monolayer catalyst.

lysts, residuals of vanadium(V) ions were remaining in the solution, possibly, due to the equilibrium between the precipitated and the aqueous vanadate species. This equilibrium could be shifted towards the formation of surface vanadium/alumina compounds at low concentrations of vanadium due to the predominance of the vanadium adsorption process.

3.2. Infrared (IR) studies

Table 2 lists the IR data of different V_2O_5/Al_2O_3 catalysts as well as those of Al_2O_3 and V_2O_5. An IR band at 1023 cm⁻¹ was displayed by catalysts of monolayer or higher vanadium content and also by V_2O_5. This band is assigned to the stretching vibration of V=O [17,18,28,29]. As for catalysts of vanadium content less than the monolayer composition they did not exhibit the 1023 cm⁻¹ band, therefore, they did not possess vanadyl group.

The IR data of ammonia adsorbed on the calcined catalysts are also listed in Table 2. The data of ammonia adsorbed on Al_2O_3 and V_2O_5 are also included in this Table. The V_2O_5/Al_2O_3 catalysts as well as Al_2O_3 itself always exhibited strong peaks around 3500 and 1650 cm⁻¹ due to H_2O adsorption, thus we focused on the spectra in the region below 1600 cm⁻¹ in the following results and discussion.

The IR spectrum of NH_3 adsorbed on Al_2O_3 exhibited one absorption band at 1253 cm⁻¹ due to coordinatively held NH_3 to Lewis acid sites [11,14,17,18,30–33]. It is documented that Al_2O_3 does not possess Brønsted acidity, in accordance with our results. In the IR spectrum of the monolayer catalyst as well as in those of lower vanadium content, the band of the coordinately held ammonia (1235 cm⁻¹) and another band at 1450 were displayed. The latter band is assigned to NH_3 adsorbed on Brønsted acid sites of vanadia adsorbed on alumina [11,17,18,29–33]. The intensity of the 1235 cm⁻¹ band, for coordinately held NH_3, decreased gradually with vanadium coverage, until it vanished completely for the $AV_{5.21}$ catalyst. In the meantime, these catalysts exhibited another IR band at 1420 cm⁻¹. This band is assigned to the adsorption of NH_3 on Brønsted acid sites located on particles of V_2O_5 precipitated on Al_2O_3 surface [11,17,18]. There is a strong correlation between the appearance of the 1420 cm₋₁ IR absorption band and the dissolution of the V_2O_5/Al_2O_3 catalysts in NH_3 (Table 1 and Table 2), indicating the formation of V_2O_5 particles due to precipitation on Al_2O_3 surface at high loadings of vanadium. As crystalline V_2O_5 does not possess Lewis acidic sites [11,33], therefore the disappearance of the 1235 cm⁻¹ IR absorption band for $AV_{5.21}$, after adsorbing NH_3, indicates complete coverage of $V_2O_5/$
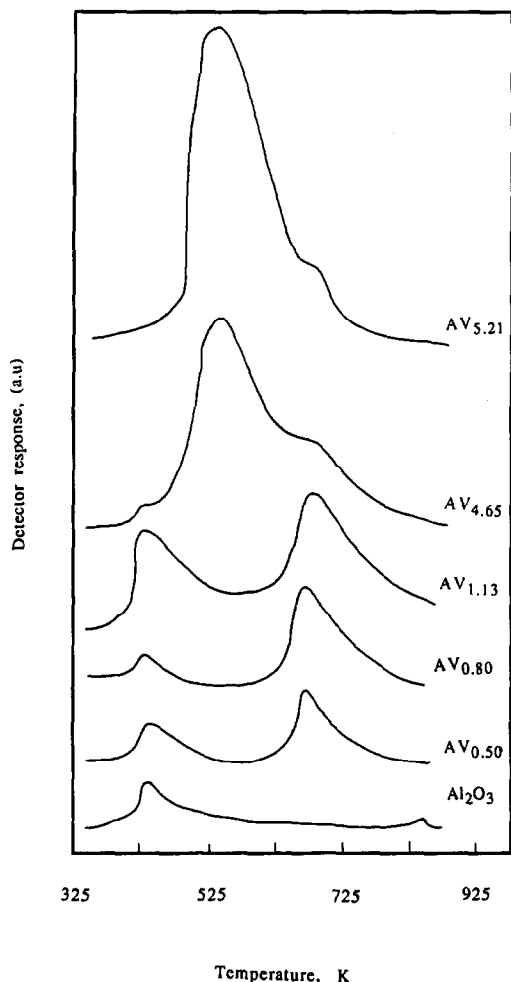
Fig. 1. Temperature programmed desorption ammonia profiles for alumina and vanadia–alumina catalysts.

Al_2O_3 surface with particles of crystalline V_2O_5. This is further proof for the formation of V_2O_5 precipitates on V_2O_5/Al_2O_3 surface.

3.3. Thermal programmed desorption (TPD)

Fig. 1 shows the relationship between the thermal conductivity of the desorbed NH_3 and the linear increase in temperature for Al_2O_3 as well as for different V_2O_5/Al_2O_3 catalysts. The TPD profile of Al_2O_3 is characterized by one strong NH_3 desorption peak at ≈ 440 K and a weaker peak at ≈ 810 K. These two peaks were assigned to the desorption of coordinately held NH_3 from Lewis acid sites of different strength [14]. Table 3 shows that the number of Lewis acid sites on Al_2O_3 is 2.8×10^{14} site cm^{-2}. This value is comparable to the literature value (3.38×10^{14} site cm^{-2} [14]).

In the TPD spectra of catalysts of vanadium content lower than the monolayer coverage ($AV_{0.50}$ and $AV_{0.80}$), the intensities of the 440 K NH_3 desorption peak have decreased and the peak at 810 K has completely vanished. Furthermore, an intense peak for NH_3 appeared at ≈ 640 K. The 440 K NH_3 desorption peak is assigned, as in the case of Al_2O_3, to desorption from Lewis acid sites, while the other peak at 640 K is attributed to the desorption of NH_3 from Brønsted acid sites of vanadium oxide adsorbed on alumina. This was further supported by IR results of these catalysts after desorbing NH_3 by heating at 503 K and then,

Table 3
Numbers of different acidic sites on V_2O_5/Al_2O_3 catalyst as determined by quantifying the desorbed NH_3

Catalyst	Lewis acid site $cm^{-2} \times 10^{14}$ [a]	Brønsted acid site on adsorbed vanadia $cm^{-2} \times 10^{14}$ [b]	Brønsted acid site on crystalline V_2O_5 $cm^{-2} \times 10^{14}$ [c]
Al_2O_3	2.8	0.0	0.0
$AV_{0.50}$	2.1	5.1	0.0
$AV_{0.80}$	1.4	7.1	0.0
$AV_{1.31}$ [d]	3.4	7.6	0.0
$AV_{4.65}$	0.4	5.2	15
$AV_{5.21}$	0.0	4.1	22

[a] As determined by quantifying the desorbed NH_3 at 503 K, via the trichloramine method [23], and assuming that each NH_3 molecule was bound to a Lewis acid site.
[b] As in the case of footnote a but heating at 723 K.
[c] As in the case of footnote a but heating at 563 K.
[d] The monolayer catalyst.

at 723 K. These results showed complete disappearance of the 1235 cm^{-1} infrared band of the coordinately held NH_3 by heating at 503 K, while the NH_4^+ IR band (1450 cm^{-1}) disappeared by heating at 723 K.

The number of different acidic sites is shown in Table 3. From this table it is clear that the number of Lewis acid sites is less than the case of Al_2O_3; revealing that some of these sites are covered with V-oxide. Furthermore, the ratio of Brønsted acid sites to V atoms is 2.8 and 2.2 in the case of $AV_{0.50}$ and $AV_{0.80}$ catalysts, respectively. These ratios indicate that most of the vanadia species were in the form of isolated vanadyl groups, as each isolated vanadyl species could have three O–H groups. For the monolayer catalyst, although the Al_2O_3 surface was covered with more V-oxide in comparison to $AV_{0.50}$ and $AV_{0.80}$ catalysts, the intensity of the 440 K TPD peak, characterizing the desorption of the coordinately held NH_3, has unexpectedly increased. It is thus suggested that NH_3 was coordinately bound to unsaturated vanadium ions as well as to uncovered Al ions. These vanadium ions could be regarded as Lewis acid sites [12]. Indeed the IR spectrum of the monolayer catalyst, Table 2, displayed an IR absorption band at 1023 cm^{-1} assignable to the stretching vibration of vanadyl groups of the monolayer catalyst. Regarding the Brønsted acid sites on the monolayer catalyst, a value of 1.4 Brønsted acid site/V is predicted from Tables 1 and 3. This is a low value compared to those of the lower vanadium loadings catalysts. As the vanadium content was increased, the degree of polymerization of the surface vanadyl species would do likewise. Therefore, according to the structure of the catalyst in scheme 1, the OH groups of the vanadyl species, which were responsible for the Brønsted acidity, would be consumed in forming the V–O–V bridges of the polymeric surface species. Therefore, as suggested in Scheme 1, at very high values of *n*, the degree of polymerization, which increased with the increase in vanadium loadings, the ratio of OH groups to V atoms would decrease due to the consumption of V–OH species during polymerization.

As vanadium loading was increased, the TPD peak of coordinatively held NH_3 was decreased and completely vanished for $AV_{5.21}$ catalyst. In the meantime, an ammonia TPD shoulder was displayed at ≈ 530 K. The decrease in the Lewis acid activity with the increase in the vanadia loadings is in accordance with the enhanced formation of crystalline V_2O_5 which exhibits only Brønsted acidity [11,33]. In order to probe the nature of this shoulder, IR spectra of the high vanadium loadings catalysts ($AV_{4.65}$ and $AV_{5.21}$) were taken, before, and after, desorbing NH_3 by heating at 563 K for 20 min. Before desorbing NH_3, an IR band at 1425 cm^{-1} was exhibited. This band is therefore assignable to NH_3 adsorbed on V–OH species of the precipitated vanadium pentoxide [11,17,18]. Moreover, this IR band has disappeared by heating, at 563 K. Therefore, the TPD shoulder at 530 K could be assignable to NH_3 desorbed from Brønsted acid sites of crystallite V_2O_5 precipitated on Al_2O_3 carrier.

4. Conclusion

(i) Vanadium oxide of low vanadium loadings resisted dissolution in an ammoniacal solution due to strong bonding to the Al_2O_3 support via Al–O–V and V–O–V bridges. On the other hand, at higher vanadium loadings, particles of crystalline V_2O_5 were precipitated on Al_2O_3, and thus dissolved in NH_4OH solution.

(ii) The low vanadium loading catalysts exhibited Brønsted acidity due to V–O–H species and Lewis acidity due to uncovered Al ions. In addition to these sites, the monolayer catalyst exhibited Lewis acidity assignable to unsaturated vanadium ions.

(iii) Catalysts of high vanadium loadings exhibited two kinds of Brønsted acidity assignable to V–OH species of adsorbed V-oxide on Al_2O_3, and V–OH species of crystalline V_2O_5, whereas Lewis acidity was diminished due to coverage of the catalyst surface with particles of V_2O_5.

Acknowledgements

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