Reactivity of V_2O_5/MgF_2 catalysts for the selective ammoxidation of 3-picoline

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V_2O_5/MgF_2 catalysts with V_2O_5 contents ranging from 2.1 to 15.7 wt% were prepared, and the influence of the V_2O_5 content of the V_2O_5/MgF_2 catalyst on the structure and activity for the ammoxidation of 3-picoline was investigated. XRD data indicate that V_2O_5 is in a highly dispersed state though segregation of V_2O_5 into tiny crystallites occurs at and above 8 wt% V_2O_5. The 3-picoline ammoxidation activity increased with an increase in V_2O_5 content due not only to the species arising out of interaction of V_2O_5 and MgF_2, but also to the presence of V_2O_5 microcrystals in the catalysts.

KEY WORDS: ammoxidation; 3-picoline; nicotinonitrile; V_2O_5/MgF_2 catalysts.

1. Introduction

In the recent past, we investigated the ammoxidation of 3-picoline over vanadia catalysts on different supports [1–5]. The selective ammoxidation of 3-picoline in terms of high nicotinonitrile productivity was achieved on the monolayer (3.4 mol% V_2O_5/TiO_2) catalyst [1,2]. Ammoxidation of 3-picoline isomers depends not only on the physico-chemical characterstics of the catalysts, but also on the molecular structures of picolines [3]. 4-Picoline with methyl group farthest from the nitrogen atom is more favorably adsorbed and converted into its corresponding nitrile than the other two picoline isomers. CeF_3 has been found to give a highly active and selective 3-picoline ammoxidation catalyst when a higher amount of vanadia (~15 wt%) was deposited on it [4]. The activity of the catalyst was attributed to a new $CeVO_4$ phase formed by the interaction of vanadia with the CeF_3 surface when the catalyst was calcined at 723 K in air. The steric effect in ammoxidation of picolines was also observed on highly active titania-supported ceria catalysts [5]. MgF_2 as a support has been reported for a number of transition metal oxide catalysts [6–10]. However, V_2O_5/MgF_2 has not yet been investigated for the ammoxidation of 3-picoline.

In this communication, we report on the results of a preliminary investigation of the role played by MgF_2 support in influencing the activity and selectivity of V_2O_5/MgF_2 catalysts with varying V_2O_5 contents for the ammoxidation of 3-picoline.

2. Experimental

2.1. Catalyst preparation

MgF_2-supported vanadia catalysts with V_2O_5 contents ranging from 2.1 to 15.7 wt% were prepared by a wet impregnation technique by contacting MgF_2 (Loba Chemie, India) particles (18 to 25 BSS mesh) with a requisite amount of NH_4VO_3 (Aldrich, USA) dissolved in aqueous oxalic acid solution [1]. The excess water in the impregnated samples was evaporated to dryness on a water bath. The samples were then oven dried at 393 K for 16 h and finally calcined at 723 K for 6 h. Vanadia contents in the catalysts were estimated by an atomic absorption spectrometer (Perkin-Elmer, Model 2380) after decomposing the samples in aquaregia and preparing solutions in the required concentration range.

2.2. Catalyst characterization

XRD patterns of the calcined V_2O_5/MgF_2 catalysts were recorded on an X-ray diffractometer (Philips PW-1140) using nickel-filtered Cu K_α radiation. The BET surface area (S_{BET}) and NH_3 chemisorption capacities of the catalysts were measured in an all-glass high vacuum system capable of attaining pressures of 10^{-6} torr. Surface areas of the catalysts were determined by N_2 adsorption at 77 K. The NH_3 chemisorption capacities of the catalysts were carried out at ambient temperature after calcined catalysts were degassed at 423 K for 2 h [3].

2.3. Catalyst activity

The activity of the catalysts for ammoxidation of 3-picoline was determined following the procedure described in

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an earlier publication [1]. Briefly, the reaction is carried out over a 2 g catalyst in a fixed-bed reactor operating under atmospheric pressure at a reaction temperature of 633 K with a feed ratio of 3-picoline : water : ammonia : air = 1 : 13 : 6 : 44 (mole ratio). The liquid (3-picoline + water) flow is maintained at 2 ml/h.

3. Results and discussion

The BET surface areas and NH_3 uptakes of V_2O_5/MgF_2 catalysts are presented in table 1. MgF_2 has a surface area of 98 $m^2 g^{-1}$. The surface areas of all the catalysts are much lower than that of MgF_2. When MgF_2 is reduced in H_2 at 723 K, its surface area decreases from 98 to 64.6 $m^2 g^{-1}$. The surface areas of the calcined catalysts decrease from 35.7 to 24.1 $m^2 g^{-1}$ when the V_2O_5 content is raised from 2.1 to 15.7 wt%. V_2O_5 has a surface area of 6 $m^2 g^{-1}$, which, after reduction in H_2 at 640 K, appears to have become porous and increased to 25.3 $m^2 g^{-1}$. The large decrease in the surface area of the support upon loading with 2.1 wt% V_2O_5 may be attributed to pore blocking. With a further increase in V_2O_5 loading to 5.7 wt%, the decrease in the surface area is relatively low (from 35.7 to 28.4 $m^2 g^{-1}$). When V_2O_5 loading is further increased to 8 wt% and beyond the decrease is only marginal. This behavior indicates that probably a V_2O_5 monolayer on MgF_2 is formed at the loading of 2.1 wt% itself and above 2–3 wt% V_2O_5/MgF_2 V_2O_5 microcrystals started forming. MgF_2 and V_2O_5 have adsorbed 564 and 63 μmoles g^{-1} of ammonia respectively at ambient temperature. Even though the ammonia uptake is higher on MgF_2 compared to that of V_2O_5, the surface density of ammonia for MgF_2 is lower than that of V_2O_5. When 2.1 wt% V_2O_5 is deposited on MgF_2, the resulting catalyst has adsorbed less ammonia than that of MgF_2; however, the surface density of the sites is higher on this catalyst than that of pure MgF_2. With a further increase in V_2O_5 loading from 2.1 to 15.7 wt% ammonia chemisorption capacities increase from 274 to 767 μmoles g^{-1}. It appears that the V_2O_5 microcrystals are more capable of adsorbing ammonia on their Brønsted acid sites than on surface V_2O_5 sites on MgF_2, which may primarily be Lewis acid sites that are not kinetically efficient in adsorbing ammonia. As the number of these Brønsted acid sites increases with increase in V_2O_5 loading, ammonia uptake also increases.

Table 1
BET surface areas (S_{BET}) and NH_3 uptakes of V_2O_5/MgF_2 catalysts.

V_2O_5/MgF_2 (V_2O_5 wt%)	S_{BET} ($m^2 g^{-1}$)	RTAC[a] (μmol g^{-1})	RTAC[a] (μmol m^{-2})
2.1	35.7	274	7.68
5.7	28.4	385	13.56
8.0	27.8	451	16.22
10.3	26.8	540	20.15
15.7	24.2	767	31.69
Pure MgF_2	98.1	564	5.749
Pure V_2O_5	6.0	63	10.50

[a] Room temperature ammonia chemisorption.

The XRD patterns of the calcined V_2O_5/MgF_2 catalysts (figure 1) contain highly intense XRD reflections (d = 3.26, 2.24, 1.73, 1.40, 2.08, 1.65, 2.54 and 1.54 Å) characteristic of the MgF_2 support. The intensity of these reflections decreased slightly with an increase in V_2O_5 loading up to 8 wt%, indicating that the surface of the support is getting progressively covered with the molecular structures of V-oxides [9]. The XRD pattern of 8 wt% V_2O_5 catalyst contains a lone weak XRD reflection (d = 4.38 Å), indicating the presence of V_2O_5 crystallites. However, in the catalysts with lower than 8 wt% V_2O_5 loading, the presence of V_2O_5 microcrystals with a diameter of <4 nm is possible. The intensities of XRD reflections of V_2O_5 (d = 4.38, 3.40 and 2.88 Å) though weak are enhanced slightly with an increase in V_2O_5 content from 8 wt% onwards. Even at 15.7 wt% V_2O_5 loading these intensities are low, indicating the presence of mainly V_2O_5 microcrystals only.

The influence of V_2O_5 content on ammoxidation of 3-picoline over reduced V_2O_5/MgF_2 catalysts is shown in figure 2. The 3-picoline conversion increases at a faster rate from 16.7 to 65% when the V_2O_5 content of the catalysts is increased from 2.1 to 8 wt%, and thereafter at a slower rate up to 90.7% as the V_2O_5 loading is further increased to 15.7 wt%. Pyridine selectivity decreases from 8.9% at 2.1 wt% V_2O_5 loading to 2.3% at 15.7 wt% V_2O_5 content in the catalysts. It may be noted that nicotinonitrile selectivity has increased considerably from 87.1 to 96.4% with an increase in V_2O_5 loading from 2.1 to 15.7 wt%. The 15.7 wt% V_2O_5/MgF_2 catalyst with the highest nicotinonitrile selectivity of 96.4% at the highest 3-picoline conversion of 90.7% would give the highest yield of 3-cynopiridine (87.4%) under the specified reaction conditions employed in this study. These observations indicate that nicotinonitrile formation is taking place on active vanadia species of the V_2O_5/MgF_2 catalyst, the number of which are increasing with V_2O_5 loading (interacting V_2O_5 and V_2O_5 microcrystals) and demethylation of 3-picoline to pyridine is perhaps occurring mostly on acidic sites of MgF_2 support. It appears that the acidic sites (mainly Brønsted acid sites) associated with V_2O_5 microcrystals that adsorb ammonia are active for the ammoxidation reaction and do not catalyze the demethylation of 3-picoline. The formation of pyridine is suppressed as the surface of the support is progressively getting covered with molecular structures of V-oxides [9,11,12] as the vanadia content of the catalyst is increased. Jonson *et al.* [13] reported the formation of benzene in ammoxidation of toluene over V_2O_5/Al_2O_3 catalysts and attributed the demethylation to the acidic sites on the γ-Al_2O_3 support.

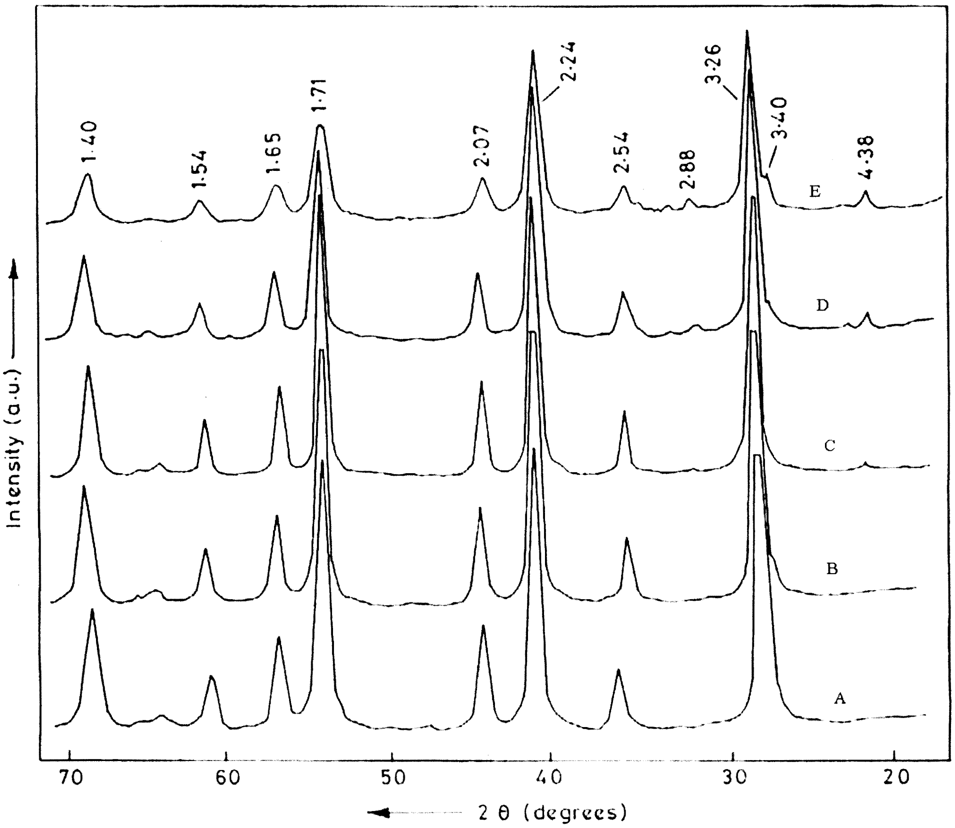

Figure 1. XRD patterns of V_2O_5/MgF_2 catalysts with various V_2O_5 loadings. A—2.1 wt%, B—5.7 wt%, C—8.0 wt%, D—10.3 wt%, E—15.7 wt%.

According to Haber *et al.* [9] at low V_2O_5 loadings on MgF_2 support, (V:O) F_5-type surface complexes and isolated VO_4 tetrahedra which transform to chains of tetrahedra of the metavanadate type are formed. At higher vanadia concentrations polyvanadate species with octahedrally coordinated vanadium are deposited at the surface. Thus, in the range of V_2O_5 loadings studied, the catalysts pass through various forms ranging from dispersed isolated species to oligomers and finally to crystalline phases. Haber and Wojciechowska [8]

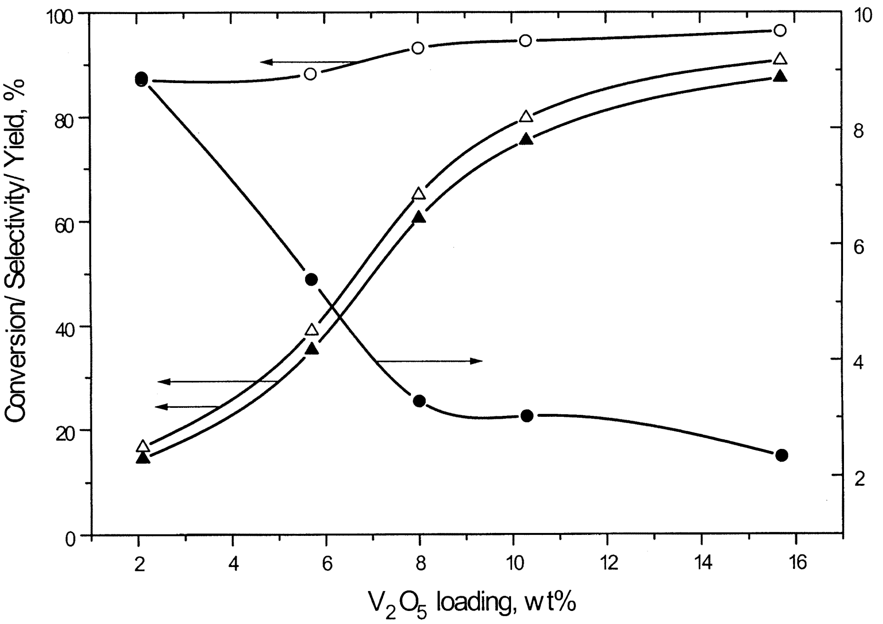

Figure 2. Influence of V_2O_5 loading on MgF_2 for the ammoxidation of 3-picoline. △, 3-picoline conversion; ○, nicotinonitrile selectivity; ▲, nicotinonitrile yield; ●, pyridine selectivity.

have shown that the highest ammoxidation of toluene occurred at the monolayer coverage of V_2O_5/MgF_2 catalysts. The ammoxidation of 3-picoline is believed to involve the redox cycle of V-oxides on V_2O_5/MgF_2 catalysts just as in oxidation reactions [14]. We observed that the reduced V_2O_5/MgF_2 catalysts attained steady-state ammoxidation activities within 4 h of time on stream and the activities were found to be stable during the entire 24 h period of time on stream studied. At a reaction temperature of 633 K the amount of unidentified products is less than 1.5%. It may be mentioned here that the performance of this catalyst (selectivity of 96.4% at a conversion of 90.7%) is much superior to that of the monolayer (3.4 mol%) V_2O_5/TiO_2 catalyst (selectivity of 95% at a conversion of 70%) reported by us earlier [1]. From these results it may be inferred that the interacted species and microcrystals of V-oxides in the reduced MgF_2-supported V_2O_5 catalysts are very stable and active in the presence of a large quantity of water vapor that is added to the reactants and produced during the course of the reaction, like those present when V_2O_5 catalysts on oxide supports are used [11]. The surface VO_x species and V_2O_5 microcrystals on MgF_2 provide sites for adsorption and activation of oxygen and ammonia respectively, for participation in the ammoxidation reaction after reduction. The use of a large quantity of water vapor (molar ratio of 3-picoline : $H_2O = 1:13$) appears to have effectively suppressed oxidation of ammonia to N_2 [15] and oxidation of 3-picoline to CO_2 [16]. Jehng *et al.* [12] have observed by LASER Raman spectroscopy that the hydrolysis of V-oxides at elevated temperatures (>503 K) does not occur to a significant extent and the surface V_2O_5 species are stable on the oxide supports in the presence of moisture.

4. Conclusions

Deposition of V_2O_5 on a non-conventional acidic support, MgF_2, gave a highly active, selective and stable catalyst for ammoxidation of 3-picoline to nicotinonitrile. The V_2O_5/MgF_2 catalyst with ~16 wt% V_2O_5 loading exhibited high nicotinonitrile selectivity at a high 3-picoline conversion, giving a nicotinonitrile yield of >87% at a reaction temperature of 633 K, 3-picoline : water : ammonia : air mole ratio of 1 : 13 : 6 : 44 and W/F of 5.4 gh/mole.

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