Studies on rejuvenation of spent residue hydroprocessing catalysts by leaching of foulant metals: influence of inorganic salt additives on the leaching efficiency of organic acids

M. Marafi, A. Stanislaus and C.J. Mumford[1]

Petroleum Technology Department, Petroleum, Petrochemicals and Materials Division, Kuwait Institute for Scientific Research (Kuwait), PO Box 24885, 13109 Safat, Kuwait

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A comparative study has been made on the efficiency of oxalic, malonic and acetic acids for selective removal of metal foulants (e.g. vanadium) from spent residue hydrotreating catalysts in the presence and absence of aluminium nitrate. The influence of concentration of the added salt (aluminium nitrate) on the leaching efficiency of the three acids was also studied. The treated catalysts were characterized and the improvements in surface area, pore volume and HDS activity as a result of leaching with each reagent compared. The studies revealed that addition of aluminium nitrate enhanced the leaching efficiency of each acid to a different degree. The rate of vanadium leaching by oxalic acid was increased substantially by aluminium nitrate addition whereas for acetic acid there was only a moderate enhancement in leaching rate. The enhanced leaching by the aluminium nitrate–organic acid system may be explained in terms of a synergistic mechanism involving oxidizing and complexing reactions. The improvement in surface area and pore volume achieved on rejuvenation were related to the extent of removal of vanadium from the catalyst. The HDS activity of the catalyst was also increased significantly by leaching of the deposited metals. The selectivity for vanadium leaching (V/Mo ratio) was found to be an important factor for HDS activity recovery.

Keywords: Rejuvenation; hydroprocessing catalyst generation; metal leaching

1. Introduction

Upgrading of heavy oils and residues to more valuable products by catalytic hydroprocessing has achieved considerable importance worldwide in recent years. Heavy oil feeds contain high concentrations of impurities, e.g., sulfur, nitrogen, vanadium, nickel and asphaltenic compounds. The high metal concentration and coking tendency of heavy residues reduce considerably the life of hydroprocessing

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[1] Department of Chemical Engineering and Applied Chemistry, Aston University, Birmingham, UK.

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catalysts. The catalysts are found to deactivate rapidly as a result of deposition of coke and metals [1–3].

Currently deactivated catalysts are not regenerated and reused, but are discarded as solid wastes. Catalyst dumping may lead to environmentally unacceptable leaching of toxic metals [4,5]. Metal recovery from spent catalyst is possible, but is uneconomic due to the low price of the recovered material [6]. Therefore, clearly it is desirable to regenerate and reuse the spent catalyst, since it would have potential economic and environmental advantages.

The regeneration of the deactivated catalysts presents a major technological challenge in the field of residue hydroprocessing. Regeneration by conventional procedures, using nitrogen–air or steam–air under controlled conditions, does not result in complete reactivation of the catalyst. Carbon is removed completely, but metallic impurities remain on the catalyst and act as a diffusion barrier for the reactants. Therefore, to rejuvenate metal-fouled residue hydroprocessing catalysts it is necessary to remove metal foulants by leaching with chemical reagents.

Several processes have been described in the literature for the removal of metals from residue hydrotreating catalysts by chemical treatment [7,8]. Organic and inorganic acids have been used as reagents for metal leaching [9–11]. However, the influence of inorganic salt additives on the leaching efficiency of organic acids has received little attention [8,12]. In the leaching of metals by organic complexing agents, the addition of inorganic salts may change the complexing character and greatly affect the leaching efficiency. In the present work a comparative study has been made on the efficiency of three different acids, namely, oxalic, malonic and acetic acid for selective leaching of metal foulants from spent residue hydrotreating catalysts. The influence of adding an inorganic salt, e.g. aluminium nitrate, on the leaching efficiency of each acid is also examined. The effect of concentration of the added salt has also been studied. The spent and treated catalysts have been characterized by different techniques and improvements in surface area, pore volume and HDS activity of the catalysts as a result of leaching with different reagents are compared.

2. Experimental

Spent catalyst was obtained from the atmospheric residue hydrodesulfurisation unit of Kuwait National Petroleum Company (KNPC). For consistency the spent catalysts for all the experimentation was collected from one batch. They were in spherical form and contained residual oil, sulfur, carbon, vanadium and nickel deposits in addition to the catalyst metals (Co and Mo) originally present (table 1). The contaminated residual oil was removed by thoroughly washing with naphtha in a mechanical shaker. The cleaned catalyst was then dried in an oven at 120°C for 24 h.

Table 1
Characteristics of fresh and spent catalyst

Catalyst property	Fresh catalyst	Spent catalyst
carbon (wt%)	0.00	11.10
sulfur (wt%)	0.00	8.34
vanadium (wt%)	0.00	15.10
nickel (wt%)	0.00	3.70
cobalt (wt%)	2.58	1.10
molybdenum (wt%)	7.81	4.00
iron (wt%)	0.00	0.18
sodium (wt%)	0.00	0.10
surface area (m^2/g)	203	44
pore volume (ml/g)	0.71	0.14
average diameter	1.44	1.52
side crushing strength (N/pellet)	39.00	34.00
bulk density	0.72	1.31

BDH, analytical reagent grade oxalic, malonic and acetic acids (concentration 0.66 molar) were used as extracting reagents. Leaching experiments were conducted in a fixed bed laboratory glass reactor. The reagent was pumped continuously through the catalyst bed from the bottom of the reactor (up-flow), at a flow rate of 3 ℓ/h. The liquid product was collected in the reagent vessel and circulated continuously through the catalyst bed for the requisite periods of time. The concentrations of various metals (V, Ni, Mo and Co) present in the leach liquid and catalyst samples were determined by inductively coupled argon plasma (ICAP) spectroscopy. The surface areas of the catalysts were determined by nitrogen adsorption (BET method) using a Quantasorb adsorption unit manufactured by Quantachrome Corporation, USA.

Activity tests were conducted in a fixed bed microreactor using 5 ml catalyst charge. Atmospheric gas oil containing 2 wt% sulfur was used as feed. The operating conditions were: pressure 40 bar; temperature 350°C; H_2/oil ratio 400 ml ml^{-1} h^{-1}; LHSV 6 h^{-1}. The catalyst samples were presulfided in the reactor before use. The presulfiding procedure involved passing 3 wt% CS_2 in atmospheric gas oil over the catalyst which was maintained at 300°C and 40 bar pressure. The LHSV was adjusted to 6 h^{-1} and presulfiding was continued for 3 h. A Princeton Gamma Tech. model 100 sulfur analyser was used to measure the sulfur content in the feed and product.

The catalyst activity was calculated as relative volume activity (RVA) compared to the fresh catalyst activity [13]. The fresh catalyst was considered as the reference standard with RVA = 100. The RVA was defined as follows:

$$\mathrm{RVA} = \frac{k_{\mathrm{sample}}}{k_{\mathrm{standard}}} \mathrm{RVA}_{\mathrm{standard}} ,$$

where k is the reaction rate constant. The value of k was calculated using the equation

$$k = \mathrm{LHSV}\frac{1}{n-1}\left(\frac{1}{S_{\mathrm{p}}^{n-1}} - \frac{1}{S_{\mathrm{f}}^{n-1}}\right),$$

where LHSV is the liquid hourly space velocity (ml ml^{-1} h^{-1}); n is the reaction order; S_{f} is the sulfur in feed wt%; S_{p} is the sulfur in product, wt%.

From literature, it is known that the reaction order for different feedstocks varies between 1 and 2. For atmospheric gas oil reaction order variations from 1.3 to 1.7 and for vacuum gas oil between 1.5 and 1.9 have been reported [13]. For our atmospheric gas oil (AGO) test, a value of $n = 1.5$ was used.

3. Results and discussion

3.1. EFFECT OF ALUMINIUM NITRATE ON THE LEACHING EFFICIENCY OF DIFFERENT ACIDS

Leaching studies were conducted with oxalic, malonic and acetic acids in the presence and absence of aluminium nitrate. Figs. 1–3 illustrate the influence of aluminium nitrate addition on the efficiency of the three acids for vanadium removal. These demonstrate that the rate of vanadium leaching by oxalic acid is increased significantly by aluminium nitrate addition (fig. 1) but there is no appreciable improvement for malonic acid (fig. 2). A moderate enhancement in the leaching rate is observed for acetic acid (fig. 3). A similar effect of aluminium nitrate

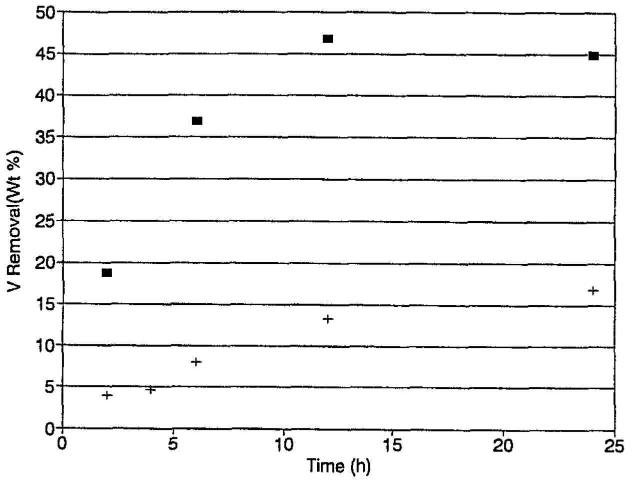


Fig. 1. Effect of oxalic acid with (■) and without (+) $Al(NO_3)_3$ on V removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.

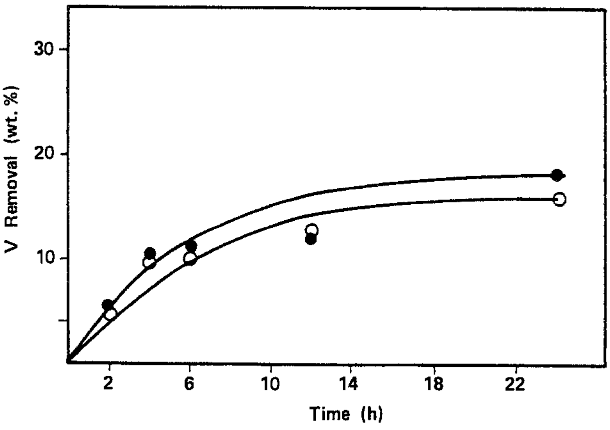


Fig. 2. Effect of malonic acid with (●) and without (○) $Al(NO_3)_3$ on V removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.

addition is also shown for nickel extraction by each acid (figs. 4–6). It is relevant to consider the various steps involved in the leaching process in order to explain the observed difference in leaching behaviour.

The process of leaching normally involves the following individual steps: (a) diffusion of leaching reagent to the solid liquid interface, (b) reaction between the solid and the reagent to form a product, (c) dissolution of the product, and (d) diffusion of the dissolved product away from the interface. Any combination of the above steps may control the rate of leaching and the amount of material leached.

In spent hydrotreating catalysts, the metals are present as sulfides [14]. In such systems, the leaching reactions can be expected to be of the overall form:

$$MS_2 + 4CH_3COOH \rightarrow M(-OOC \cdot CH_3)_4 + 2H_2S,$$

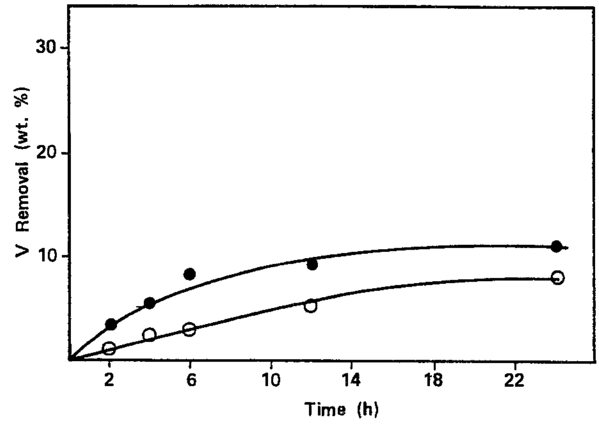


Fig. 3. Effect of acetic acid with (●) and without (○) $Al(NO_3)_3$ on V removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.

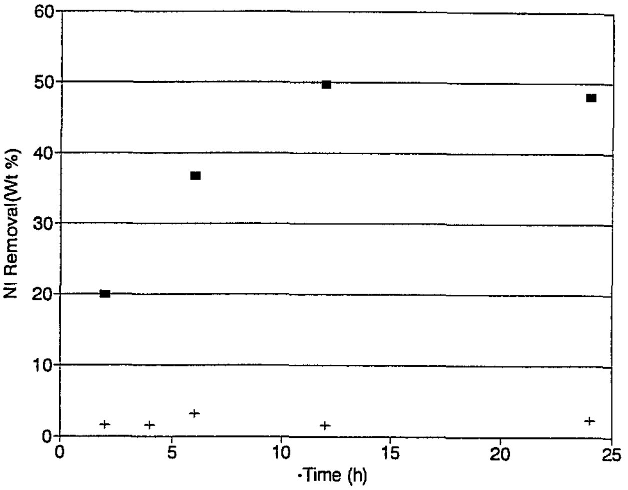
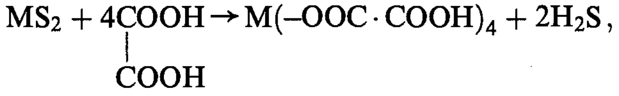
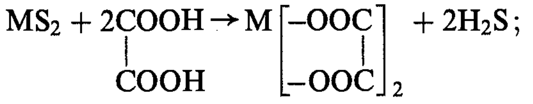


Fig. 4. Effect of oxalic acid with (■) and without (+) $Al(NO_3)_3$ on Ni removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.



$$\mathrm{MS_2} + 4\underset{\displaystyle \mathrm{COOH}}{\underset{|}{\mathrm{COOH}}} \rightarrow \mathrm{M(-OOC\cdot COOH)_4} + 2\mathrm{H_2S},$$

or



$$\mathrm{MS_2} + 2\underset{\displaystyle \mathrm{COOH}}{\underset{|}{\mathrm{COOH}}} \rightarrow \mathrm{M}\begin{bmatrix}\mathrm{-OOC}\\ | \\ \mathrm{-OOC}\end{bmatrix}_2 + 2\mathrm{H_2S};$$

in aqueous systems, such reactions can be expected to proceed in three stages,

$$4\mathrm{CH_3COOH} \rightarrow 4\mathrm{CH_3COO} + 4\mathrm{H^+},$$

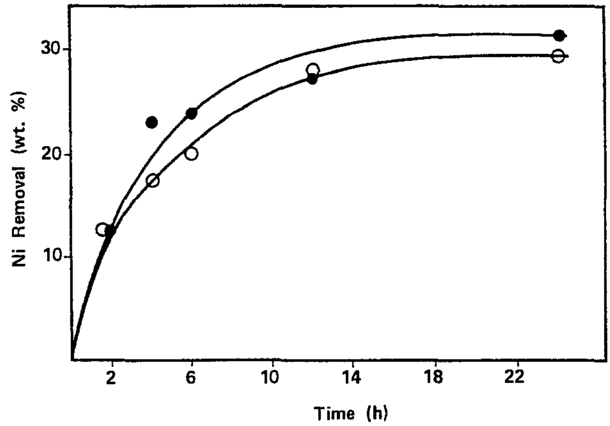


Fig. 5. Effect of malonic acid with (●) and without (○) $Al(NO_3)_3$ on Ni removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.

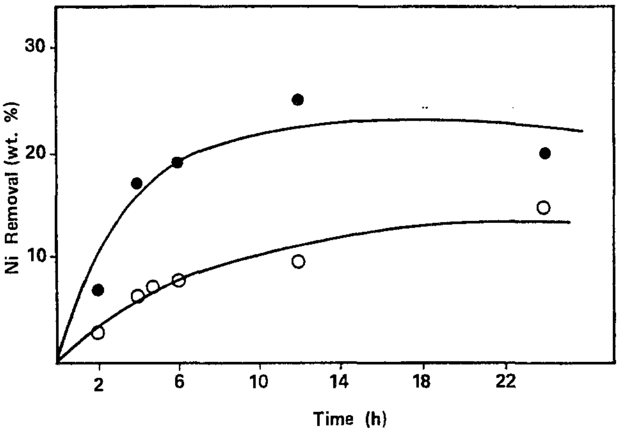


Fig. 6. Effect of acetic acid with (●) and without (○) $Al(NO_3)_3$ on Ni removal. Acid concentration = 0.66 M; aluminium nitrate concentration = 1 M.

$$MS_2 + 4H^+ \rightarrow 2H_2S + M^{4+},$$

$$M^{4+} + 4CH_3COO^- \rightarrow M(OOCCH_3)_4,$$

which will be controlled by the ionization constants of the acids, by the production of metal ions and by the production of the metal complex.

The ease of formation of the metal ion, its reaction with the complexing agent and dissolution of product depend to a large extent on the oxidation state of the metal in the metal compound. As mentioned earlier, the metals in the spent catalysts are predominantly present in the form of low-valent sulfides [14,15]. The role of aluminium nitrate in enhancing the leaching by the acid reagents is probably to oxidize the low-valent metal sulfides to higher oxidation states which may be more easily attacked by the acid reagent. Alternatively, aluminium nitrate may enhance the ability to wet and transport the organic leaching agent through the carbon overlayer.

The oxidation mechanism with nitrate ion serving as an oxidant appears more likely. Brown fumes of nitrogen oxides were observed during leaching with oxalic acid–aluminium nitrate reagent. Furthermore, addition of alternative salts such as aluminium sulfate to oxalic acid did not enhance leaching activity [8].

In agreement with this, in oxidized catalyst samples leaching was substantially higher even in the absence of aluminium nitrate and addition of aluminium nitrate to the acid had no appreciable effect (table 2). Thus, a synergistic effect involving oxidizing and complexing appears to be responsible for the enhanced leaching by the aluminium nitrate–oxalic acid system. The observed difference in the enhancement of the rate of leaching of vanadium and nickel for different acids with aluminium nitrate may be attributed to the difference in the ionization of the acid,

Table 2
Effect of oxalic acid with and without aluminium nitrate and oxidized spent catalyst

Reagent	Metal removal (wt%)	
	V	Ni
oxalic acid	42	44
oxalic acid + $Al(NO_3)_3$	40	44

leading to formation of metal ions and the solubility of the product (metal complex).

Metal complexes of organic acids such as $[VO(oxalate)^{2-}]$ and $[VO(ac)_4]^{2-}$ have been observed under different conditions [16]. Accurate identification of the products of the reactions was beyond the scope of the present study but the nature of the products obtained by leaching would be of considerable interest for further study.

Experiments were also conducted to find the optimum concentration of aluminium nitrate promoter for leaching of contaminant metals. Only oxalic acid was used in the study as it was considered the most promising reagent for removal of contaminant metals. Fig. 7 shows the effect of aluminium nitrate concentration in the reagent mixture (oxalic acid–aluminium nitrate) on the leaching of vanadium and nickel. It is interesting to note that an increase in aluminium nitrate concentration from 0.1 to 0.5 M leads to a substantial improvement in the extent of leaching of both vanadium and nickel. Further increase in the concentration of aluminium nitrate has no appreciable effect on the extraction of both metals. Since the role of aluminium nitrate in enhancing the leaching is to oxidize the metals to higher oxida-

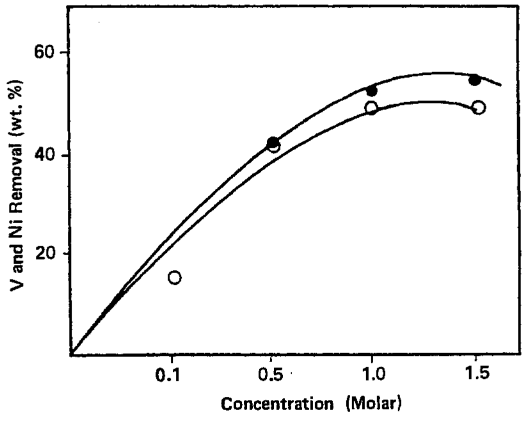


Fig. 7. Effect of $Al(NO_3)_3$ concentration on V (○) and Ni (●) removal, using oxalic acid. Acid concentration = 0.66 M. At 12 h; T = 25°C.

tion states, its promotional effect would be expected to be limited to its reaction stoichiometry with metal ions, which is in turn limited by the accessibility of metal ions to the reagents. At concentrations above 1 M, the amount of aluminium nitrate appears to be in excess of that required on the basis of chemical stoichiometry, so that the rate of leaching reaction is zero order with respect to the aluminium nitrate.

3.2. EFFECT OF METAL LEACHING WITH DIFFERENT REAGENTS ON CATALYST SURFACE AREA, PORE VOLUME AND HDS ACTIVITY

The surface area, pore volume and HDS activity of the catalyst samples treated with each acid both with and without aluminium nitrate were determined in order to examine the improvement in these properties as a result of removal of the contaminant metals. The results are presented in table 3. The amount of vanadium leached and ratio of leached V/Mo for each reagent as well as the surface area and pore volume of untreated spent catalyst and the corresponding fresh catalyst are also included in table 3.

The results show that the surface area and pore volume for the spent catalyst decreased from 203 m^2/g and 0.71 ml/g to 44 m^2/g and 0.14 ml/g respectively, due to metal deposition on the pores of the catalyst. After oxalic acid treatment for about 12 h the surface area, and pore volume of spent catalyst were increased to 87.6 m^2/g and 0.20 ml/g respectively. Significant improvement in these properties also occurred with malonic acid treatment. However, the increase was less pronounced with acetic acid. The activity data presented in table 3 demonstrate that the catalyst activity is improved significantly by leaching of the deposited metals. Samples treated with oxalic acid/promoter and malonic acid/promoter show a large increase in HDS activity compared with those treated with the acid without

Table 3
Relation between vanadium removal, V/Mo ratio, surface area, pore volume and HDS activity

Sample	Vanadium leached (wt%)	Ratio of V/Mo leached	Surface area (m^2/g)	Pore volume (ml/g)	HDS activity (wt%)	RVA
fresh catalyst	–	–	203	0.71	54	100
spent catalyst	–	–	44	0.14	30	41.1
leached with oxalic acid	17.4	0.96	88	0.20	28	37.8
leached with oxalic acid +$Al(NO_3)_3$	46.0	1.76	125	0.31	45	73.4
leached with malonic acid	15.9	5.1	86.0	0.21	42	66.0
malonic acid+$Al(NO_3)_3$	18.4	15.4	110	–	48	81.5
acetic acid	7.9	0.9	56	0.1	33	46.7
acetic acid+$Al(NO_3)_3$	11.0	0.47	85	0.15	34	48.7

promoter. The results indicate that the improvement in catalyst activity is directly related to the increase in surface area and pore volume.

In the case of the sample treated with malonic acid + $Al_2(NO_3)_3$, it is noticed that about 80% of the activity can be regenerated by removing about 1/5 of vanadium. Some explanation of this observation can be advanced in terms of the location of vanadium in the spent catalyst and its role in catalyst deactivation. Electron microprobe analysis of the spent catalyst used in our studies showed that high concentrations of vanadium were near the outer edge of the catalyst pellet [8]. Such large accumulations may block the pore mouths. It is generally agreed that the residue hydrotreating catalysts are predominantly deactivated by pore mouth plugging [3,17].

Leaching of the vanadium deposits from the pore mouths should open the pores and consequently increase the surface area of the catalyst. The improvement in surface area is particularly high up to about 20% vanadium removal and this might probably explain the high activity recovery by the removal of about 1/5th of the total vanadium deposited on the catalyst. It appears that less than 20% of the total vanadium deposited on the catalyst pellet was responsible for pore mouth plugging and obstruction of much of the catalyst surface.

The results presented in table 3 also reveal that the selectivity for V removal (V/Mo ratio) is an important factor for HDS activity recovery. Thus for example, in the case of malonic acid, although the amount of vanadium removed is not as high as in the case of oxalic acid, the HDS activity of the catalyst is improved significantly. This is probably due to high selectivity for V removal (V/Mo=15.4) for the malonic acid + aluminium nitrate reagent system.

4. Conclusions

The addition of aluminium nitrate was found to enhance the leaching efficiency of each acid to a different degree. Thus, the rate of vanadium leaching by oxalic acid was increased remarkably by aluminium nitrate addition, whereas for malonic acid there was no appreciable improvement. With acetic acid there was only a moderate enhancement in leaching rate. The enhanced leaching by the aluminium nitrate–organic acid system may be explained in terms of a synergistic mechanism involving oxidizing and complexing reactions.

The treated catalysts were characterised and improvements in surface area, pore volume and HDS activity as a result of leaching with each reagent compared. The improvements in surface area and pore volume achieved by leaching were related to the extent of removal of vanadium from the catalyst. Improvement in surface area is particularly high upto about 20% vanadium removal. The HDS activity of the catalyst was also increased significantly by leaching of the deposited metals. The selectivity for vanadium leaching (V/Mo ratio) was found to be an important factor for HDS activity recovery.

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