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Studies of a new alkene oligomerization catalyst derived from nickel sulfate

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Abstract

$NiSO_4/\gamma$-Al_2O_3 shows very high catalytic activity in alkene oligomerization with good selectivity for dimers. Its acidity plays a very important role in the catalytic behavior. However, it is the acid site with an acid strength of $H_0 \leq -3.0$ that is related to the oligomerization of alkenes. Comparatively strong acidity is produced through the interaction of sulfate anions and γ-Al_2O_3 during calcination. Ni(II) is partially reduced to Ni(I) by reacting with ethene and propene at ambient temperature or evacuation at high temperatures. Dimerization of ethene can be considered as coordination catalysis at active sites of Ni(I), while oligomerization of propene proceeds via dual catalysis due to both coordination catalysis and acid catalysis. But-1-ene is catalytically oligomerized via mainly acid catalysis. Thus, it can be concluded that as the number of carbon atoms of the alkenes increases, the mechanism of oligomerization of the alkene over the catalyst shifts from coordination catalysis to acid catalysis. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alkene oligomerization; Nickel sulfate; Ni^+; Acid site; Acid catalysis; Coordination catalysis

1. Introduction

Catalytic oligomerization of lower alkenes to synthesize higher alkenes has attracted much attention of investigators. Synthesis of higher alkenes is of special importance in the chemical and oil refining industries. Through dimerization or oligomerization of ethene by organic transition metal compounds, such as those of Al, Ni, Ti, etc. as catalysts, C_4–C_{18} alkenes have been prepared on an industrial scale as intermediates in the production of detergents, LLDPE, plasticizers and lube oil additives [1]. There has been a history of 50 years in producing polymer gasoline through phosphoric acid oligomerization of alkenes derived from gaseous products of cracking petroleum distillates [2]. As an excellent catalyst in alkene oligomerization, ZSM-5 has aroused the interests of researchers. Products of highly branched higher alkenes have been synthesized, from which different relative amounts of high-octane gasoline and diesel fuel range products can be obtained. Hydrogenation of the latter gives diesel oil with high cetane number [3].

The discovery of nickel-based heterogeneous catalysts for alkene oligomerization dates back to the 1930s. Morikawa [4] first found that nickel deposited on Kieselguhr could catalyze dimerization of ethene at room temperature. Research on nickel-based heterogeneous catalysts for alkene oligomerization has been actively carried out for the past 60 years. Attention has been mostly paid to oligomerization of lower alkenes, such as ethene or propene, on NiO–SiO_2 [5–11], NiO–

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SiO_2–Al_2O_3 [12–17], Ni^{2+} exchanged amorphous $SiO_2 \cdot Al_2O_3$ [18,19], NiO–Al_2O_3/SiO_2 [20–22], Ni^{2+} zeolites [23–27], etc.. In early works, research focused on the important role played by the acid sites of the catalyst, but extensive studies on nickel component have also been conducted, especially on the oxidation state of Ni. Different postulates concerning the oxidation state of the nickel have been advanced. In comparing these with the catalyst in homogenous coordination catalysis Feldblium [28] considered nickel hydride to be the active sites on Ni-based heterogeneous catalysts. Other authors [20,29] maintained that coordinated unsaturated Ni^{2+} serves as active sites. Ni^0 was also taken as the active site by some other authors [23]. Ozaki and coworkers [9,30] held the opinion that the active site responsible for ethene dimerization consists of low valent nickel ions and an acid. Elev et al., through the study on the dimerization of ethene on NiCaY catalyst, concluded that the activity of the catalyst was controlled by the number of Ni^+ ions, which could be precursors of the catalytically active intermediates. Many workers have found that Ni^+ can be produced from Ni^{2+} in different chemical state, such as Ni/SiO_2 [31,32], Ni/Al_2O_3 [24], NiCaX [32], etc. at 77 K in a hydrogen atmosphere through UV assisted reduction or mild heating reduction, and the reduced catalysts showed enhanced activity in the oligomerization of ethene or propene. Furthermore, these catalysts are liable to be poisoned by CO. From these facts, the conclusion that Ni^+ constitutes the active site on the catalyst can be drawn. Nevertheless, it can hardly be said that the controversy over the nature of the active sites of nickel-based heterogeneous catalysts for alkene oligomerization has been settled.

In this paper, $NiSO_4$/γ-Al_2O_3, a new member of the series of Ni-based heterogeneous alkene oligomerization catalyst was investigated. $NiSO_4$ is a kind of solid acid [33]. When loaded on γ-Al_2O_3, η-Al_2O_3, $SiO_2 \cdot Al_2O_3$ and SiO_2, it exhibits extraordinary activity in the oligomerization of alkenes, which is similar to the action of the above-mentioned Ni-based solid catalysts for alkene oligomerization [34,35]. Extensive studies were made on the effect of the acidity of the catalyst and the valence state of Ni on the activity of the catalyst. Differences in behavior of various alkenes – ethene, propene and but-1-ene and differences in mechanism of their catalytic oligomerization on the catalyst are also intensively studied. In this paper, the results obtained in past several years are summarized and a new topic in progress is briefly introduced.

2. The surface structure of the catalyst and its catalytic behavior

$NiSO_4$/γ-Al_2O_3 catalyst was prepared by incipient wet impregnation of 40–60 mesh γ-Al_2O_3 with an aqueous solution of $NiSO_4$, and calcination at 773 K in a stream of dry air. Examination of the phase structure of the resulting catalyst by XRD shows that the diffraction pattern is similar to that of γ-Al_2O_3 when the amount of loading does not exceed 8 wt% of Ni. A tiny diffraction peak of the hexagonal crystal of $NiSO_4$ is detected when the amount of loading reaches 9 wt% of Ni [36]. Through quantitative phase determination by XRD, the threshold (the maximum amount of monolayer dispersion) [37] was found to be 0.27 g $NiSO_4$/g-γ-Al_2O_3, which corresponds to 8.2 wt% of Ni [38]. This result is in agreement with the surface morphology obtained through TEM studies. Hence it can be considered that with 8 wt% of Ni loading, $NiSO_4$ covers the surface of γ-Al_2O_3 as a monolayer. The amount of loading expressed in wt% of Ni on the catalyst showing maximum activity in the oligomerization of ethene, propene and but-1-ene are 5–10, 2.5–10 and 8, respectively [36,39,40]. It follows that a catalyst possesses maximum activity when $NiSO_4$ is distributed as a monolayer on its surface. More loading than required for monolayer distribution will cause the formation of double layers of $NiSO_4$ on the catalyst and lower the catalytic activity, since the catalytic activity of pure $NiSO_4$ under similar reaction conditions is almost negligible.

The reactivities of ethene, propene, and but-1-ene in closed circulating system are shown in Fig. 1. Their sequence of reactivity is as follows [41,42]:

ethene > propene > but-1-ene

$NiSO_4$/γ-Al_2O_3 catalyst possesses characteristics of exceedingly high activity and high selectivity for dimers at low reaction temperatures. Oligomerization

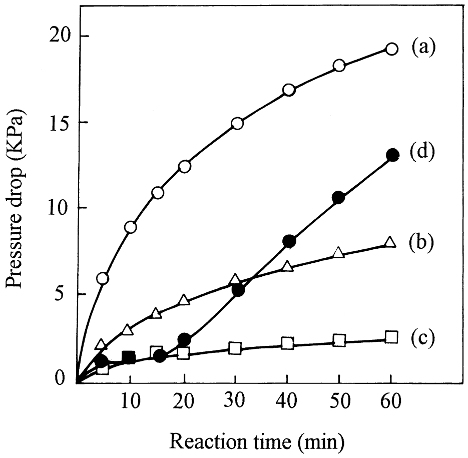

Fig. 1. Alkene oligomerization over a $NiSO_4/\gamma\text{-}Al_2O_3$ catalyst. Reaction temperature: 303 K. (a) Ethene; (b) propene; (c) but-1-ene over catalyst evacuated at 773 K for 4 h; and (d) ethene over the catalyst calcined in O_2 at 773 K for 4 h and followed by outgassing at room temperature.

of propene over $NiSO_4/\gamma\text{-}Al_2O_3$ catalyst under conditions of $T=273$ K, $P=2.5$ MPa and LHSV=1 h^{-1} gives a conversion and the dimerization selectivity as high as 90% and 82%, respectively. When the reaction temperature was increased to 303 K, the conversion reached 98%, while the dimerization selectivity decreased to 62% [36]. Under conditions of $T=353$ K, $P=2.5$ MPa and LHSV=2 h^{-1}, the conversion of *n*-butene was 85.4%, and its product was mainly the dimer [40]. Such a high activity in alkene oligomerization can hardly be attained on ordinary solid acid catalysts.

3. Acidity of supported catalysts

3.1. *Effect of support*

The support has a dramatic effect on the activity and acidity of the catalyst, as illustrated in Table 1. It is shown that catalysts supported on $\gamma\text{-}Al_2O_3$, $\eta\text{-}Al_2O_3$, $SiO_2{\cdot}Al_2O_3$ and SiO_2 are characterized by the presence of acid sites of $H_0\leq-3.0$ and high catalytic activity [43,44]. These characteristics of the supported catalysts are in agreement with the conclusion of Sohn and Ozaki [11] in their study of the dimerization of ethene on montmorillonite ($NiO{\cdot}SiO_2$) where activity is correlated roughly with the acidity of $H_0\leq-3.0$.

3.2. *Effect of calcination temperature on acidity of the catalyst*

Catalyst acidity determined by Hammett indicators and irreversible adsorption of NH_3 methods showed a pronounced dependence on the calcination temperature and reaches a maximum value when the calcination temperature ranges from 773 to 873 K [36,40]. It was suggested that strong acid sites were generated by the interaction between the sulfate anion and $\gamma\text{-}Al_2O_3$. Too high a calcination temperature may induce the transformation of $\gamma\text{-}Al_2O_3$ crystallinity or decomposition of sulfate anion, resulting in the simultaneous lowering of catalyst acidity and activity.

3.3. *NaOH poisoning*

Acid sites on solid catalyst are generally neutralized by exposure to basic compounds, such as NaOH, NH_3,

Table 1
Activities for alkene oligomerization and acidities of $NiSO_4$ catalysts supported on various supports

Support	Activity			Acidity (mmol/g-cat.)				
	Ethene (mmol/g-cat. 10 min)	Propene (conv., %)	But-1-ene (conv., %)	$H_0\leq-3.0$	$H_0\leq+1.5$	$H_0\leq+3.3$	$H_0\leq+4.8$	$H_0\leq+6.8$
$\gamma\text{-}Al_2O_3$	5.20	94.3	85.4	0.35	0.55	0.85	1.05	1.45
$\eta\text{-}Al_2O_3$	5.90	94.0	–	0.55	0.65	0.85	1.15	1.45
$SiO_2{\cdot}Al_2O_3$	4.50	90.0	56.0	0.25	0.45	0.55	1.15	1.45
SiO_2	1.03	30.0	45.9	0.15	0.15	0.15	0.55	0.55
TiO_2	0	0	25.6	0	0	0	0.01	0.03
La_2O_3	–	0	4.0	0	0	0	0.04	0.04
Fe_2O_3	0	0	–	–	–	–	–	–

Loading: 1.0 mmol $NiSO_4$/ml-support. Reaction conditions – ethene: $T=283$ K, P(init.)=26.7 MPa; propene: $T=283$ K, $P=2.5$ MPa, LHSV=1 h^{-1}; but-1-ene: $T=353$ K, $P=2.5$ MPa, LHSV=2 h^{-1}.

pyridine etc.. To clarify the role of acid sites in the reaction, the poisoning of acid sites was performed by impregnation of the catalyst with NaOH solution, and subsequent calcination of the catalyst was carried out. It was considered that the strongest acid sites will be neutralized first.

Through NaOH treatment, the distribution of acid sites was altered and the activity of the catalyst was lowered, as shown in Figs. 2 and 3. From these figures, it can be seen that when the amount of NaOH is around 0.85 mmol/g-cat., the acid sites of $H_0 \leq -3.0$ disappear, and meanwhile the catalytic activities in the oligomerization of ethene, propene and but-1-ene fall nearly to 0 [41–43,45]. From this fact it can be concluded that the acid sites which are directly related to alkene oligomerization are only those having the value of $H_0 \leq -3.0$. In the oligomerization of but-1-ene, there exists a linear relationship between catalytic activity and the acidity of $H_0 \leq -3.0$, while no such relationship is observed for ethene and propene. It is reasonable to conclude that the oligomerization of but-1-ene can be directly related to the acidity of $H_0 \leq -3.0$, while in the oligomerization of ethene and propene, another factor besides acidity of $H_0 \leq -3.0$ is responsible for the catalytic activity.

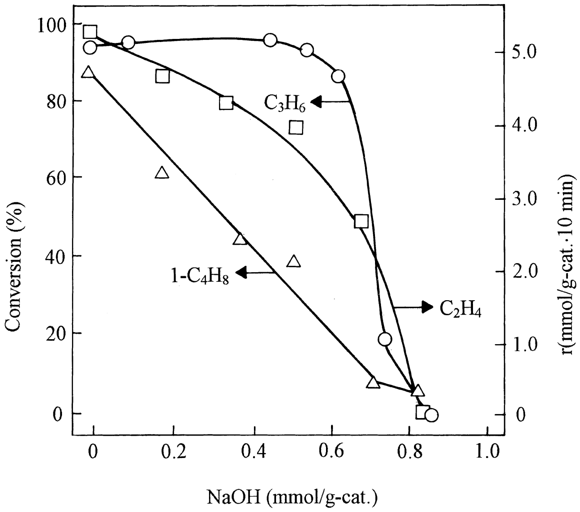

Fig. 2. Effect of NaOH poisoning of $NiSO_4/\gamma\text{-}Al_2O_3$ on alkene oligomerization. Reaction conditions: ethene, T=308 K; propene, T=283 K, LHSV=1 h^{-1}; but-1-ene T=353 K, LHSV=2h^{-1}.

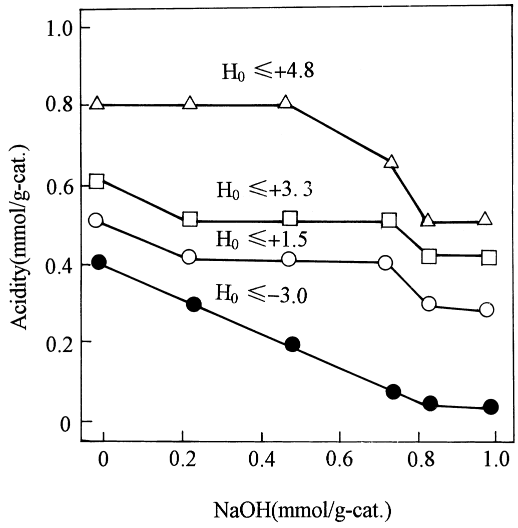

Fig. 3. Effect of NaOH poisoning on the distribution of acid strength of $NiSO_4/\gamma\text{-}Al_2O_3$ catalyst.

4. The oxidation state of nickel

4.1. Comparison between $NiSO_4$ and other sulfates

As shown in Table 2, all catalysts derived from sulfates, such as $FeSO_4$, $Al_2(SO_4)_3$, $(NH_4)_2SO_4$ etc. deposited on $\gamma\text{-}Al_2O_3$ have strong acidity and high catalytic activity for the oligomerization of propene and but-1-ene. For the oligomerization of ethene, with the exception of $Al_2(SO_4)_3/\gamma\text{-}Al_2O_3$, which is slightly active, catalysts derived from other sulfates are inactive. However, $NiSO_4/\gamma\text{-}Al_2O_3$ is highly active not only in the oligomerization of propene and but-1-ene but also in that of ethene [42]. Furthermore, its selectivity for dimers is comparable with that in homogenous coordination catalysis [46], which is characterized by high dimerization selectivity. This shows the striking difference between nickel and other counter cations in acting as a component in oligomerization catalysts.

4.2. ESR

When the catalyst was treated by evacuation at 773 K, tensor signals of $g_{\parallel}$=2.16 and $g_{\perp}$=2.08 were

Table 2
Acidity and activity for alkene oligomerization of catalysts derived from various sulfates supported on γ-Al_2O_3

	Catalyst (supported on γ-Al_2O_3)				
	$NiSO_4$	$FeSO_4$	$Al_2(SO_4)_3$	SO_4^{2-}[a]	$NiSO_4$ (CO poisoned)
Acidity (mmol NH_3/g-cat)[b]	0.688	0.631	0.348	0.230	–
Activity[c]					
Ethene (mmol/g-cat. 10 min)	5.21	0	0.90	0	0
Propene (conv., %)	98.0	56.0	26.7	30.0	53.1
But-1-ene (conv., %)	85.4	89.5	68.1	66.6	84.6
Product distribution for propene (%)					
C_6	54.5	9.52	4.17	5.50	14.9
C_9	19.7	57.0	42.3	47.2	49.7
C_{12}	23.3	25.7	38.7	35.1	25.6
C_{15}	1.86	7.76	14.1	12.2	9.84
C_{18}	0.75	0	0.72	0	0

[a] Prepared by calcination of $(NH_4)_2SO_4$/γ-Al_2O_3.
[b] Acidity determined by the procedure of ammonia irreversible adsorption at 200°C.
[c] Reaction conditions are the same as shown in Table 1.

observed [42,44,45]. This result of g values is similar to that obtained by Bonneviot et al. [47] when NiO/γ-Al_2O_3 was evacuated at 720 K, and can be assigned to Ni(I). Since $g_{\|}>g_{\perp}>g_e$, the structure of Ni(I) may be assigned to a trigonal bipyramid or a distorted octahedron coordination of $d_{x^2-y^2}$ ground state. When the catalyst is treated in a stream of oxygen and then exposed to ethene or propene at a pressure of 400 Torr (1 Torr=133.3 Pa) for 10 min, signals of $g_{\|}=2.16$ and $g_{\perp}=2.082$ also appear in the ESR spectrum registered at 77 K, as shown in Fig. 4. This proves the formation of Ni(I) on the catalyst. However, no such signals were detected when but-1-ene was introduced instead of ethene or propene. Moreover, when 600 Torr ethene is introduced to the system which has been pretreated by evacuation at 873 K, ESR signals of $g_{\|}=2.52$ and $g_{\perp}=1.975$ appeared. Under a temperature of 77 K, the change was hardly perceptible, but under room temperature, their intensity gradually decreased and finally the signals vanished [42]. This tensor is in agreement with the g value of the coordination product of ethene and Ni(I)/SiO_2 [24,26], which was prepared through the reduction of NiO/SiO_2 by UV. The difference of (a) and (d) in the dimerization of ethene illustrated in Fig. 2 shows that Ni(I) active sites may be formed either through evacuation at high temperature or the reducing action of ethene or propene. This is the reason why there is an induction period in ethene dimerization if the catalyst is calcined in oxygen atmosphere [41], as shown in Fig. 1.

4.3. IR

The oxidation state of Ni has been studied by using CO as the probe molecule. When $NiSO_4$/γ-Al_2O_3 was

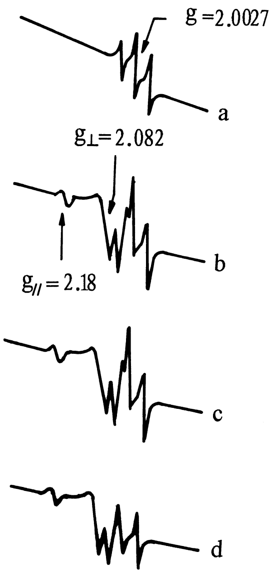

Fig. 4. ESR spectra of $NiSO_4$/γ-Al_2O_3 (at 77 K): (a) Catalyst calcined at 773 K in O_2 atmosphere for 4 h followed by vacuum treatment at room temperature; (b) introduction of ethene (600 Torr) at room temperature after (a); (c) introduction of propene (600 Torr), pretreatment are the same as (b); (d) after calcining at 773 K under vacuum for 4 h. Reprinted with permission from [45], © 1993, Elsevier Science Publishers.

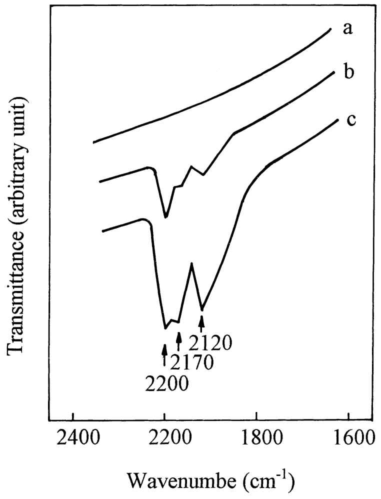

Fig. 5. IR spectra of $NiSO_4/\gamma\text{-}Al_2O_3$ calcined under vacuum: (a) Catalyst calcined at 773 K under vacuum for 4 h; (b) after the introduction of CO (40 Torr) at room temperature; and (c) after increased CO pressure to 300 Torr. Reprinted with permission from [45], © 1993, Elsevier Science Publishers.

exposed to a CO atmosphere (40 Torr), an adsorption band appeared at 2200 cm^{-1} in the IR spectrum and the band disappeared with the evacuation of the catalyst at ambient temperature [45]. This band may be assigned to the stretching vibration for the coordination of CO to Ni(II) [48]. When the catalyst was exposed to CO after the evacuation at 773 K, three adsorption bands appeared at 2200 (I), 2170 (II), and 2120 cm^{-1} (III), as shown in Fig. 5. The intensities of bands (II) and (III) increased with increasing CO pressure, while their proportions remained constant [45]. This phenomenon can be ascribed to the fact that these two bands are derived from only one species, $Ni(I)(CO)_2$. Band (II) can be assigned to a symmetrical stretch vibration and (III) to an asymmetrical stretch [27,48].

4.4. CO poisoning

Due to the fact that CO can form a stable complex with lower valent Ni(Ni(I), Ni(0)), CO can be used as the probe molecule to study the oxidation state of the active center. Catalysts such as $NiO\cdot SiO_2$ [9], Ni-exchanged zeolite [23], etc. are poisoned and completely deactivated by traces of CO. This suggests that lower valent nickel constitutes active sites. Bonneviot et al. [21] and Elev et al. [25] proved that the lower valent Ni forming the active center as suggested by Ozaki [9,30], which is actually Ni(I).

Table 2 shows that catalysts poisoned by exposing it to 40 Torr of CO completely lost activity for the dimerization of ethene. It is reasonable to believe that dimerization of ethene at Ni(I) proceeds via the coordination catalysis mechanism. In the oligomerization of propene, CO poisoning performed through exposing the catalyst to 0.2 MPa of CO caused the catalyst to lose 2/5 of its activity, and its activity and the distribution of oligomerization products became similar to those of the acid catalysts $FeSO_4/\gamma\text{-}Al_2O_3$ [41,42]. It is considered that the fraction of activity lost through CO poisoning corresponds to the contribution of coordination catalysis of Ni(I). From the above statements, it can be concluded that the oligomerization of propene proceeds via mechanisms of both coordination and acid catalysis simultaneously. CO poisoning exhibit little effect on the oligomerization of but-1-ene, which indicates that the reaction proceeds via an acid catalysis mechanism with minor contribution from coordination catalysis. It is reasonable that no ESR tensor signal of Ni(I) appeared in the case of but-1-ene. Further proof of the above deduction are given by the linear relationship between the conversion of but-1-ene and the amount of acid sites of $H_0 \leq -3.0$ [41,42].

5. Comparison between $NiSO_4/\gamma\text{-}Al_2O_3$ and Ni-exchanged $SiO_2\cdot Al_2O_3$ catalyst

From the result of the distribution of acidity on the catalyst determined by the Hammet indicators method and the quantitative relationship between the decrease of catalytic activity and NaOH poisoning in the oligomerization of ethene, propene, and but-1-ene, it was found that the lethal amount of NaOH poison of the Ni-exchanged $SiO_2\cdot Al_2O_3$ catalyst with 0.8 wt% of Ni is ca. 1.2 mmol/g-cat. The catalyst does not lose all of its catalytic activity for the oligomerization of ethene at 313 K after poisoning by exposing it to 40 Torr of CO. Its activity decreases by 81%. This indicates that the catalytic activity of oligomerization on strong acid sites cannot be ignored. The conversion of propene over a CO poisoned catalyst by exposing it to 0.2 MPa of CO, under the conditions of T=333 K, P=2.5 MPa and LHSV=1 h^{-1}, drops from 85.2% to 20.4%. In but-1-ene oligomerization, when T=363 K, P=2.5 MPa and LHSV=1 h^{-1}, CO poisoning of the catalyst reduced the conversion from 59.8% to 55.1%. A much smaller percentage of decrease in conversion of but-1-ene shows that the oligomerization of but-1-ene over Ni–$SiO_2 \cdot Al_2O_3$ mainly proceeds via acid catalysis [49]. From the CO poisoning effect on both $NiSO_4/\gamma\text{-}Al_2O_3$ and Ni-exchanged $SiO_2 \cdot Al_2O_3$ catalysts, it can be readily deduced that with the increase of the number of carbon atoms in the alkene, the mechanism of catalytic oligomerization of alkene shifts from coordination catalysis to acid catalysis; the greater the number of carbon atoms in the alkene, the more the contribution of acid catalysis is in the dual mechanism of alkene oligomerization.

6. New alkene oligomerization catalysts derived from transition metal sulfates

$Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$ catalyst prepared by the impregnation method exhibits an excellent activity in alkene oligomerization [50–53]. If a small amount of $FeSO_4$ (only 1% of the amount of $Fe_2(SO_4)_3$) is added to the $Fe_2(SO_4)_3$ solution and the catalyst is prepared by an identical procedure, activity in the propene oligomerization and the selectivity for higher oligomers of the resulting catalyst are distinctly enhanced. For example, addition of a small amount of $FeSO_4$ to an aqueous solution of $Fe_2(SO_4)_3$ causes increase in propene conversion and C_9+C_{12} oligomer selectivity from 81% and 67.2% to 95.2% and 70%, respectively, over a catalyst with 6.0 wt% Fe, under the conditions of T=323 K, P=2.5 MPa and LHSV=2 h^{-1}. The catalytic activity of the catalyst $Fe_2O_3 \cdot Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$ is higher than that of the catalyst of $Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$ having the same Fe content. From a comparative NH_3-TPD study between $Fe_2O_3 \cdot \gamma\text{-}Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$ and SO_4^{2-}/Fe_2O_3, which is considered to be a superacid [54], it has been shown that there are strong acid sites corresponding to the superacid on the former.

It has been found that the loading of catalyst $Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$ with the highest activity for propene oligomerizaton is: Fe content 6–7 wt% and at this loading it is distributed in monolayer form on the surface of $\gamma\text{-}Al_2O_3$. The lethal amount of NaOH poison was determined to be 0.91 mmol/g-cat. IR spectrum of the catalyst indicates that Lewis acid sites and Brønsted acid sites coexist on the catalyst while there is only Lewis acid sites on the surface of $NiSO_4/\gamma\text{-}Al_2O_3$ [36].

$Fe_{2/3x}Ni_{1-x}SO_4$–$P_2O_5/\gamma\text{-}Al_2O_3$ was found to be a catalyst with a high catalytic activity and stability for lower alkene oligomerizaton. When x is equal to 0.79, the catalyst of the complex salt of ferric and nickel sulfates exhibit maximum activity and selectivity. This clearly indicates the presence of the synergetic effect between different transition metal sulfates. The catalyst giving the best performance is when the weight ratio of $P_2O_5/Fe_{0.53}Ni_{0.21}SO_4$ is 0.25. NH_3-TPD study proves that additions of P_2O_5 causes the decrease in the number of strong acid sites and a simultaneous increase in the number of moderately strong acid sites. The lethal amount of NaOH is determined to be 0.72 mmol NaOH/g-cat.

7. Conclusions

$NiSO_4/\gamma\text{-}Al_2O_3$ catalyst prepared by the impregnation method, followed by calcining under non-reducing atmosphere, showed very high activity in the catalytic oligomerization of ethene, propene and but-1-ene. XRD data indicated that when the amount of loading of Ni on $\gamma\text{-}Al_2O_3$ did not exceed 8 wt%, $NiSO_4$ is homogeneously distributed in monolayer form on the $\gamma\text{-}Al_2O_3$ surface. The threshold value was found to be 8.2 wt% of Ni. Through Hammett indicator titration determination and NaOH poisoning, it has been proved that the acid sites directly related to alkene oligomerization are only those having $H_0 \leq -3.0$, and the lethal amount of NaOH poison is around 0.85 mmol/g-cat. Active sites of the catalyst for the oligomerizations of ethene, propene and but-1-ene were examined by using ESR, IR and CO poisoning of the catalyst and it can be concluded that dimerization of ethene on Ni^+ proceeds via a mechanism of coodination catalysis on Ni^+. In the oligomerization of but-1-ene, contrary to that of ethene, no Ni^+ was detected on the catalyst and CO did not cause appreciable poisoning of the catalyst. These show that oligomerization of but-1-ene mainly proceeds via the mechanism of acid catalysis. In propene oligomerization, some Ni^+ were detected on the catalyst and CO caused catalyst poisoning to a considerable extent, and the distribution of the products after CO poisoning become comparable with that in acid catalysis. Hence it is reasonable to deduce that oligomerization of propene proceeds via a binary mechanism of both coordination catalysis and acid catalysis.

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