

Study of the Poisoning of γ -Al₂O₃ by Alkali Metals Addition

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(Received 12 June 1991; revised version received 23 August 1991; accepted August 1991)

Abstract: The effect of alkali metal addition to alumina on the acid characteristics and on the isopropanol dehydration capacity was analyzed. It was found that the incidence on the catalytic and acid properties of the alkali metal doped alumina depended on the ionic radii of the added element. Thus, K produces a higher poisoning of the acid function than Na and Li. Catalytic results can be interpreted in terms of a modification of the acid sites distribution by the alkali metal addition, the stronger acid sites being mainly affected.

Key words: acidity poisoning, alcohol dehydration, alkali metals, gamma-alumina.

INTRODUCTION

The poisoning effect of the alkali metal addition to alumina has been studied by several authors, but with different interpretations about the origin of the phenomenon. Chuang and Dalla Lana¹ reported that the surface modifications and the catalytic behavior of NaOH-doped alumina can be assigned to an ion exchange between Na ions and OH groups of the alumina surface. On the other hand, Pines and Haag² indicated that the alkali metal ions added to the alumina surface poison the Lewis acid sites, whereas Jirátořá and Beránek³ found that the strong acid sites of the alumina are selectively poisoned by the sodium addition. Fiedorow and Dalla Lana⁴ reported strong evidence for the interaction of Li and Na ions with coordinatively unsaturated Al³⁺ ions, and they found that the poisoning effect upon the Lewis acid sites increases with an increase in the ionic radii of the alkali metal ion.

In this paper, the influence of the Li, Na and K addition on the acid characteristics of the γ -Al₂O₃ is studied using a test reaction such as the isopropanol dehydration, and by temperature programmed desorption of ammonia.

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EXPERIMENTAL

Alkali metal/alumina catalysts were prepared by impregnating a commercial γ -Al₂O₃ ($S = 180 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of the alkali metal hydroxide. Before impregnation, alumina was calcined at 923 K in air for 3 h. The porous structure of the γ -Al₂O₃ is defined during this calcination treatment. The alkali metal contents in the catalysts were: Li = 0.065, 0.22, 0.44, 0.72 and 1.15 mmol g⁻¹; Na = 0.022, 0.065 and 0.11 mmol g⁻¹; K = 0.013, 0.04 and 0.065 mmol g⁻¹. After impregnation, catalysts were dried at 493 K and treated in flowing H₂ at 773 K.

Samples were tested in the isopropanol dehydration reaction in a continuous flow reactor at atmospheric pressure. Alcohol was vaporized in a H₂ stream (H₂/isopropanol molar ratio = 19) and fed to the reactor with a space velocity of 0.52 mol alcohol h⁻¹ g cat⁻¹. The catalyst weight employed in all the experiments was 150 mg and the reaction temperature ranged between 423 and 673 K.

Moreover, the distribution of acid strength was determined by ammonia thermodesorption following the technique reported by Yori *et al.*⁵ Previous to the acidity measurements, the different samples were submitted to a similar treatment with H₂ at 773 K.

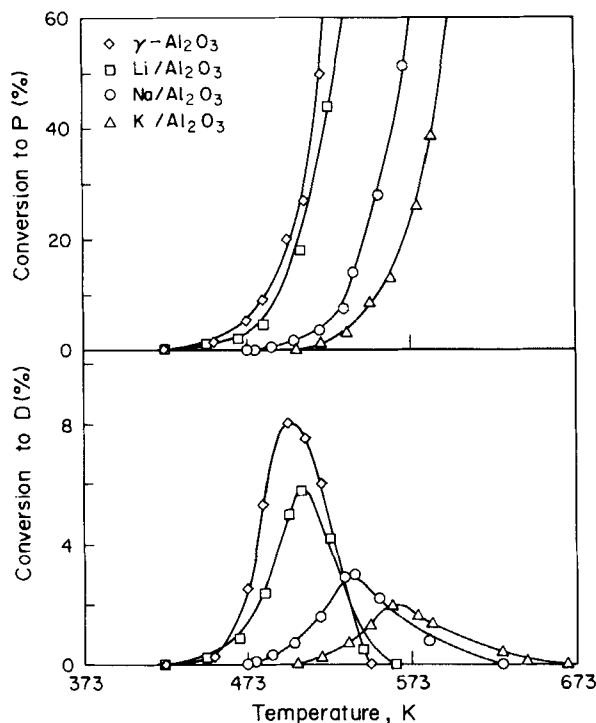


Fig. 1. Conversion to propylene (P) and di-isopropylether (D) as a function of the reaction temperature for Al_2O_3 and for $\text{Li}/\text{Al}_2\text{O}_3$, $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{K}/\text{Al}_2\text{O}_3$ with the same molar content ($0.065 \text{ mmol g}^{-1}$).

RESULTS AND DISCUSSION

In all catalytic tests the reaction products were propylene, di-isopropylether and water. Catalyst deactivation along the run was not observed and this fact can be explained by the high H_2 /alcohol molar ratio used in the tests.

Figure 1 displays the conversion of isopropanol to propylene (P) and di-isopropylether (D) as a function of the reaction temperature for Al_2O_3 , and for $\text{Li}/\text{Al}_2\text{O}_3$, $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{K}/\text{Al}_2\text{O}_3$ with the same alkali metal molar loading ($0.065 \text{ mmol g}^{-1}$). It can be observed that the conversion to propylene continuously increases with the reaction temperature. Moreover, alkali metal addition to alumina inhibits the dehydration capacity. Among the alkali-doped catalysts, $\text{Li}/\text{Al}_2\text{O}_3$ is the more active one, while $\text{K}/\text{Al}_2\text{O}_3$ displays the lowest activity. The alcohol conversion to ether shows a maximum with the reaction temperature. The intensity of this maximum decreases as follows: $\text{Li}/\text{Al}_2\text{O}_3 > \text{Na}/\text{Al}_2\text{O}_3 > \text{K}/\text{Al}_2\text{O}_3$, and it is shifted to a higher reaction temperature from $\text{Li}/\text{Al}_2\text{O}_3$ to $\text{K}/\text{Al}_2\text{O}_3$. Moreover, the shape of the propylene and ether formation curves indicates a parallel-consecutive reaction pathway, which is in agreement with other results reported in the literature.⁶⁻⁸

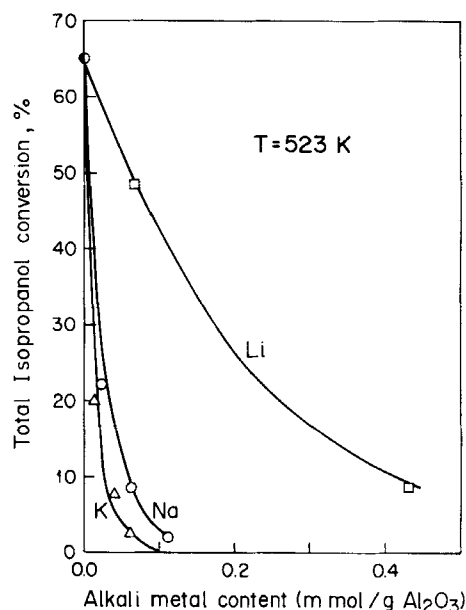
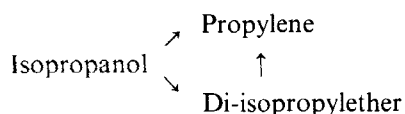


Fig. 2. Total isopropanol conversion (propylene + di-isopropylether) at 523 K as a function of the molar content of the alkali metals for $\text{Li}/\text{Al}_2\text{O}_3$, $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{K}/\text{Al}_2\text{O}_3$ catalysts.

Figure 2 shows the total conversion of isopropanol at 523 K as a function of the molar content of the alkali metal. When the additive concentration increases, the total conversion drastically drops. Furthermore, the isopropanol conversion decreases as follows: $\text{Li}/\text{Al}_2\text{O}_3 > \text{Na}/\text{Al}_2\text{O}_3 > \text{K}/\text{Al}_2\text{O}_3$. This means that the poisoning effect of the alkali metal increases with the ionic radii ($r_{\text{Li}} < r_{\text{Na}} < r_{\text{K}}$). It is also observed that the curve of conversion versus molar concentration of alkali metal shows a straight portion at low alkali content. The linear portion corresponding to $\text{Li}/\text{Al}_2\text{O}_3$ is extended in a wider range of alkali metal concentration than that of Na or K.

The influence of the alkali metal molar content on the selectivity to ether (selectivity = conversion to D/conversion to P) is shown in Fig. 3, where the reported S values were calculated at the temperatures at which the conversion to ether was at its highest. The results clearly show that the selectivity decreases as the alkali metal content increases, although this effect is higher for K than for Na or Li addition to alumina.

In addition, the above-mentioned results show that the effect of the alkali metal addition on both the activity and selectivity depends on the nature of the alkali metal, and they follow the same sequence.

The acid sites distribution is modified by the addition of high amounts of alkali metal. In fact, Table 1 shows that the density of strong acid sites decreases as the Li amount increases, whereas the density of sites of middle acidity is only affected at high Li amounts. On the other hand, the density of the weak acid sites is not practically modified by the Li addition.

In consequence, the catalytic behavior of alkali-doped

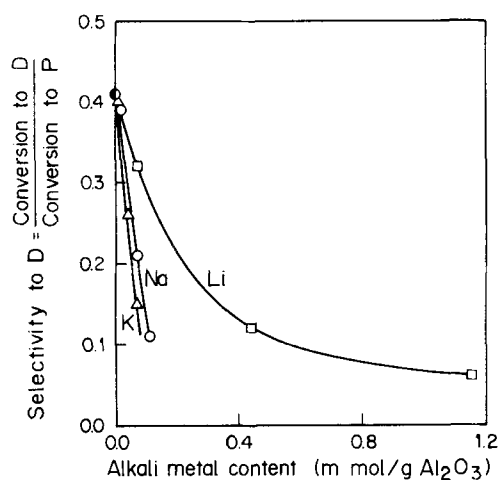


Fig. 3. Selectivity to di-isopropylether (conversion to D/conversion to P) as a function of the molar content for $\text{Li}/\text{Al}_2\text{O}_3$, $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{K}/\text{Al}_2\text{O}_3$. The reaction temperatures correspond to those at which the conversion to ether was at its highest.

TABLE 1

Acidity Distribution in $\text{Li}/\text{Al}_2\text{O}_3$ Catalysts with Different Li Contents Determined by Ammonia Thermodesorption

Li content (mmol g ⁻¹ Al_2O_3)	Amount of NH_3 desorbed (meq g ⁻¹)		
	Weak ^a	Middle ^b	Strong ^c
0	0.060	0.061	0.016
0.22	0.062	0.064	0.010
0.44	0.071	0.054	0.004
0.72	0.066	0.051	0.003
1.15	0.048	0.016	0.002

^a 473 K < T < 573 K.

^b 573 K < T < 673 K.

^c 673 K < T < 823 K.

alumina can be interpreted in terms of the modification of the acid site distribution by the alkali metal addition. Thus, activity and selectivity decrease as the poisoning of strong acid sites increases by the alkali metal addition. However, it must be taken into account that high values of isopropanol conversion to propylene can be obtained by increasing the reaction temperature in catalysts with high poisoning degree due to the alkali metal addition, as shown in Table 2. These facts indicate that the strong acid sites are involved in both the ether and the olefin formation. Taking into account that no Bronsted acidity was found on the alumina surface after calcination,⁹⁻¹⁰ the acid sites involved in the dehydration reaction are Lewis ones. According to the literature,¹¹⁻¹⁴ ether and olefin would be produced through different mechanisms: a concerted one involving an acid-basic pair (E_2 mechanism) for ether, and a one-acid site mechanism (E_1) for olefin. On this basis, the different behavior to the reaction temperature for the olefin and ether formation (when the alkali metal content increases) would indicate

TABLE 2

Reaction Temperature to Obtain the Same Isopropanol Conversion to Propylene (60%) with Different Catalysts (catalyst weight = 150 mg)

Catalyst	Alkali metal content (mmol g ⁻¹ Al_2O_3)	Reaction temperature (K)
Al_2O_3	0	518
$\text{Li}/\text{Al}_2\text{O}_3$	0.065	530
$\text{Li}/\text{Al}_2\text{O}_3$	0.44	563
$\text{Na}/\text{Al}_2\text{O}_3$	0.065	572
$\text{Na}/\text{Al}_2\text{O}_3$	0.11	594
$\text{K}/\text{Al}_2\text{O}_3$	0.04	583
$\text{K}/\text{Al}_2\text{O}_3$	0.065	595

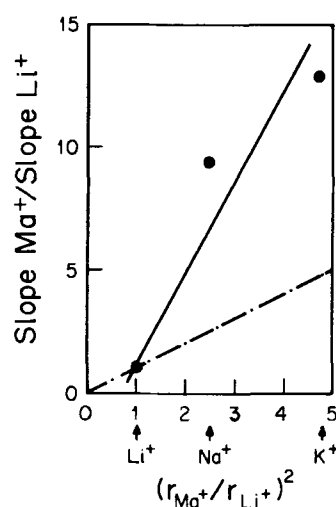


Fig. 4. Relative slope of the straight portion of the curves of Fig. 2 as a function of the square of the relative ionic radii. — — —: Theoretical straight line.

that the di-isopropylether formation takes place mainly on the stronger acid sites, whereas olefin could be produced on any acid site (weak or strong). In fact, Fiedorow *et al.*¹⁵ found a high olefin production even for Na (0.3% wt)-doped alumina, where the absence of strong acid sites was detected. Hence, when the stronger acid sites are poisoned by alkali metal addition, olefin is produced by reaction on weaker acid sites, but at a higher temperature, whereas the ether formation is inhibited.

The relative poisoning effect of Na and Li has been explained by Fiedorow and Dalla Lana⁴ on the basis that the stronger Lewis acid sites consist of more than one coordinatively unsaturated Al^{+3} , and these sites can accommodate more small ions (like Li^+) than big cations (like Na^+ or K^+). However, this explanation cannot be fully applied to the present results. In fact, taking into account Fig. 4, where the slope of the straight portion of the curves of total isopropanol conversion versus alkali metal content is represented as a function of the square

of the relative ionic radii, it can be observed that the experimental points are above the theoretical straight line. This means that the higher poisoning effect of Na and K with respect to Li is not only due to steric factors, but other effects are probably associated with the 'size' factor, although much effort is needed in order to explain this behavior.

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