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Elucidation of the zeolite role on the hydrogenating activity of Pt-catalysts

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Abstract

Toluene hydrogenation was studied over model catalysts with a fixed hydrogenating function (Pt/Al₂O₃) mechanically mixed with either HUSY or HBEA zeolites. Such mechanical mixtures showed improved platinum turnover frequencies compared to single Pt/Al₂O₃. For a same Pt content, similar activities were obtained for both zeolites catalysts indicating that the contribution of acid sites is fairly independent of the zeolite properties. Comparing to Pt-impregnated zeolite catalysts, the lower activities per site confirmed the detrimental effect of distance between Pt clusters and acid sites. Therefore, toluene hydrogenation can be used as a powerful tool to evaluate Pt-acid site intimacy in bifunctional catalysts.

Keywords: platinum; zeolite; ; bifunctional catalyst; nanoscale intimacy; toluene hydrogenation

1 Introduction

Bifunctional catalysts, namely Pt/zeolite, play a key role in modern conversion processes in industry [1-3] and most of the aspects that affect their performances have been studied along the last decades [4]. For hydrocracking catalysts, special attention has been dedicated to the metal-acid balance [5] and the degree of intimacy between both functions [6] which, nevertheless, are criteria difficult to quantify.

The difficulty of understanding fundamental phenomena occurring in complex catalytic systems can be overcome by the use of model reactions. Namely, the hydrogenation of one-ring aromatic compounds has been used to evaluate the accessibility and location of the metal sites [7, 8]. On the other hand, in the presence of acid sites (i.e. in a bifunctional catalyst) the activity can also be influenced by a support effect [9]. In most of the cases, the increased hydrogenation activity obtained over acidic supports has been attributed to the additional sites available to reactant adsorption that can be hydrogenated by spilled-over hydrogen (H_{sp}) [9, 10]. The modest sum of studies published on zeolite-based bifunctional catalysts lack systematization of clear properties-activity relationships, due to either disregard for Pt dispersion [11-13] or by holding the focus on other questions as deactivation mechanisms [8]. To fully use the potential of this model reaction on the advanced characterization of bifunctional catalysts, a background understanding of the support characteristics that affect hydrogenating activity is required.

In our previous work [14], the toluene hydrogenation was studied over Pt/zeolite catalysts based on HUSY and HBEA zeolites which are widespread in industrial catalysts. The TOF per Pt site was observed to differ by a 6-fold depending on both metal content and the support. Acknowledging the role of zeolite acidity, catalysts were evaluated by their activity per total adsorbing (metal + acid) sites which was observed to increase rapidly with $n_{Pt}/(n_{Pt}+n_A)$. A unique relationship between these two parameters was obtained for two different series of Pt/HUSY catalysts showing that the contribution of the acid sites could be well accounted by the total acidity. Comparing HBEA and HUSY catalysts, it was suggested that the proximity between Pt clusters and acid sites significantly impacted the

hydrogenating activity of the catalysts. However, it precluded the direct evaluation of the zeolite intrinsic properties on activity.

In this work, we complete our comprehensive study on properties-activity relationships by addressing the role of the zeolite on the hydrogenating activity. Therefore, toluene hydrogenation was studied over powder model catalysts with a fixed hydrogenating function (Pt/Al₂O₃) mixed with either HUSY or HBEA zeolites and the results were compared with those of HUSY and HBEA zeolites directly impregnated with Pt.

2 Experimental

Commercial zeolites HUSY (CBV720) and NH₄-BEA (CP814E) were supplied by *Zeolyst* with a global Si/Al atomic ratio of 16.7 and 13.6 respectively. NH₄-BEA zeolite was calcined to obtain the protonic form using a protocol published elsewhere [15]. Commercial Pt/Al₂O₃ in powder form was supplied by *Sigma-Aldrich* with 0.8% Pt measured by ICP-MS. Catalysts were prepared by manual milling of Pt/Al₂O₃ with either HBEA or HUSY zeolites in different proportions (see Table 1) resulting in an intimate mixture of both powders with a particle size under 200 μ m.

Table 1: Catalyst composition on Pt/Al₂O₃ and zeolite, overall Pt content and Pt/zeolite ratio.

Catalyst series	Pt/Al ₂ O ₃ (wt.%)	Zeolite (wt.%)	Pt content (wt.%)	Pt/zeolite (10 ⁻² wt/wt)
Pt/Al ₂ O ₃	100	-	0.8	-
Pt/Al ₂ O ₃ - HUSY	11	89	0.09	0.10
	33	67	0.26	0.39
	46	54	0.37	0.69
Pt/Al ₂ O ₃ - HBEA	11	89	0.09	0.10
	33	67	0.26	0.39
	46	54	0.37	0.69

Nitrogen adsorption measurements were carried out at 77 K. Total acidity was calculated from IR spectra of thermo desorbed samples at 423 K, after pyridine adsorption. Accessible Pt was determined by hydrogen titration of chemisorbed oxygen on Pt/Al₂O₃. CO chemisorption experiments were performed at room temperature, until saturation. All the

details were published in our previous paper [14]. Particle size was determined by laser granulometry using the Fraunhofer approximation with a Mastersizer 3000 (from Malvern Instruments) equipped with dry particle dispersion.

The toluene hydrogenation was performed at 383 K under atmospheric pressure with a hydrogen to toluene molar ratio of 45 over pre-reduced catalysts. Initial conversion for each catalyst was kept lower than 15% by changing the toluene space velocity. Catalytic initial activity was calculated as the toluene consumption (mmol) per catalyst gram per hour at the earliest reaction time possible ($t=1$ min). All the details were published in our previous paper [14].

3 Results and discussion

3.1 Physico-chemical properties of solids

The structural and textural properties of the three solids are depicted in Table 2. Pt/Al₂O₃ is fully mesoporous whereas zeolites are both micro and mesoporous. HBEA zeolite has a higher ~~volume of~~ mesoporous volume than HUSY, but lower microporous volume.

Table 3: Pore volumes by N₂ adsorption, concentrations of Brønsted (BAS) and Lewis (LAS) acid sites by pyridine thermodesorption followed by FTIR, Pt dispersion by H₂-O₂ titration and wavenumber of the FTIR band for Pt⁰CO species.

Sample	V _{micro} (mL g ⁻¹)	V _{meso} (mL g ⁻¹)	n _{BAS} (μmol g ⁻¹)	n _{LAS} (μmol g ⁻¹)	n _A (μmol g ⁻¹)	D (%)	n _{Pt} (μmol g ⁻¹)	vCO _{max} (cm ⁻¹)
Pt/Al ₂ O ₃	0.01	0.44	-	96	96	44	18.1	2094
HBEA	0.19	0.53	220	352	572	-	-	-
HUSY	0.33	0.20	202	87	289	-	-	-

Results in Table 2 show that HBEA zeolite exhibits two times the acid sites of HUSY (572 vs. 289 μmol/g) and six times the total acid sites of Pt/Al₂O₃. Both zeolites report similar concentration of BAS (200 – 220 μmol/g) and so the main difference is the 4-fold higher LAS concentration of HBEA (350 vs. 90 μmol/g).

Concerning adsorption of CO followed by FTIR, IR bands in the region 2150 – 2000 cm^{-1} result from CO stretching mode when linearly adsorbed onto Pt^0 surface atoms [16] which for $\text{Pt}/\text{Al}_2\text{O}_3$ is a single band centred at 2094 cm^{-1} . For Pt supported in the same zeolites used in this study, the contribution of Pt^0 is centred at 2097 cm^{-1} [14] and so, in our case of study, Pt clusters have similar electronic density. The mean particle size of Pt clusters on Al_2O_3 estimated through metal dispersion is around 2.2 nm which fits within the same range of particle size for Pt dispersed on HUSY and HBEA zeolites estimated before: 1.8-3.0 nm [14].

3.2 Toluene hydrogenation

Catalysts were obtained by intimate mixture of HUSY or HBEA zeolite with $\text{Pt}/\text{Al}_2\text{O}_3$ in different proportions (see Table 1). The composition of the mixtures ~~were~~was chosen to cover a range of Pt/zeolite weight ratio from 0.001 to 0.007² as used in a previous work [14]. Catalytic results are summarized on Table 3.

Table 3: Hydrogenating to adsorbing sites ratio, activity, turnover frequency and activity per total adsorption sites at t=1 min, and deactivation rate at t=60 min.

Catalyst series	Pt content (wt.%)	$n_{\text{Pt}}/(n_{\text{Pt}}+n_{\text{A}})$	A ($\text{mmol h}^{-1} \text{g}^{-1}$)	TOF_{Pt} (10^3h^{-1})	$A/(n_{\text{Pt}}+n_{\text{A}})$ (h^{-1})	Deactivation @ 60 min (%)
$\text{Pt}/\text{Al}_2\text{O}_3$	0.8	0.158	15.0	0.83	131	60
$\text{Pt}/\text{Al}_2\text{O}_3$ - HUSY	0.09	0.008	1.8	0.86	7	90
	0.26	0.026	9.8	1.65	42	83
	0.37	0.040	14.1	1.69	68	92
$\text{Pt}/\text{Al}_2\text{O}_3$ - HBEA	0.09	0.004	3.0	1.48	6	77
	0.26	0.015	10.3	1.67	25	52
	0.37	0.024	12.0	1.40	34	43

Focusing the discussion on the catalytic initial activities (at t=1 min), the turnover frequencies of platinum (TOF_{Pt}) for the all set of catalysts vary from 800 to 1700 h^{-1} . Zeolite-based catalysts have significantly higher TOF_{Pt} than $\text{Pt}/\text{Al}_2\text{O}_3$ individual catalyst and so improved activity per metal site. In literature, the enhancement of one-ring aromatics hydrogenation activity has been related to the presence of acid sites through the hydrogenation of reactant molecules that are adsorbed on these additional acidic sites by

spilled over hydrogen (H_{sp}) [9, 10]. In our previous work on Pt/zeolite catalysts [14], TOF_{Pt} varied by 6-fold depending on both metal content and zeolite structure. To account the contribution of the acid sites, it was suggested to consider the activity per total number of adsorbing sites. This activity was shown to increase rapidly with the ratio of hydrogenating to adsorbing sites, $n_{Pt}/(n_{Pt}+n_A)$.

Concerning the deactivation rate, all catalysts exhibit important deactivation which has been reported in literature as being due to the plugging of micropores by “coke” molecules derived from toluene [8]. In the same way, the lower deactivation of HBEA-based catalysts could be due by the higher percentage of mesoporous volume compared to HUSY ones.

3.3 Effect of Pt location

Figure 1 shows the evolution of the activity per adsorbing site with $n_{Pt}/(n_{Pt}+n_A)$ for Pt/HUSY, Pt/HBEA, Pt/ Al_2O_3 -HUSY and Pt/ Al_2O_3 -HBEA. For a given ratio, the activity per adsorbing site of Pt-impregnated zeolite catalysts is higher than that of Pt/ Al_2O_3 mixed with zeolite and its activity is also more sensitive to n_{Pt} compared to zeolite series mixed with Pt/ Al_2O_3 .

The comparison in Figure 1 accounts the differences on catalysts in terms of total acidity by n_A and Pt dispersion by n_{Pt} . In the same way, Pt clusters have been shown to be similar in all catalyst series regarding electronic properties and particle size. Thus, the differences on the activities per adsorbing site cannot be explained by Pt and acid sites intrinsic properties. As a matter of fact, a pronounced difference between catalysts, that is not being accounted, is the location of Pt: in impregnated catalysts, the Pt is directly dispersed on the zeolite whereas, in mechanical mixtures, the zeolite is Pt-free. Taking into account the dispersion of Pt on HUSY and HBEA, a maximum Pt-acid site distance can be estimated between 30 to 70 nm, by assuming an homogeneous Pt distribution inside the zeolites. On the contrary, for a mechanical mixture composed mainly by zeolite, the maximum Pt-acid site distance can be estimated by Pt/ Al_2O_3 granulometry. For our sample, the (volume weighted) mean diameter-mean is 57 μm . Therefore, direct impregnation of Pt on zeolites provided a Pt-acid

site distance in the nanoscale whereas only a mesoscale intimacy could be obtained by mechanical mixture.

The detrimental effect of Pt-acid site distance on the activity per adsorbing site agrees with the hypothesis formerly formulated that the rate of H_{sp} supplied to the adsorbing sites is the limiting step on the contribution of acid sites to hydrogenation activity [14]. The higher inter-site distance leads to a longer diffusion pathway, diminishing the rate of H_{sp} supplied to the acid sites and, consequently, the activity per acid site. In the same way, the proximity between Pt clusters and OH groups in HBEA impregnated catalysts was proposed to be also the key parameter to their higher activity for similar $n_{Pt}/(n_{Pt}+n_A)$ comparing to HUSY ones [14].

3.4 Zeolite role on Pt/Al₂O₃-based catalysts

We established that the contribution of acid sites is much lower when the Pt-acid site distance is increased, but, nonetheless, zeolites contribute to the hydrogenating activity of Pt sites deposited on Al₂O₃. This can be verified by the significantly higher TOF_{Pt} of Pt/Al₂O₃-zeolite catalysts comparing to Pt/Al₂O₃ alone (see Table 3), i.e. similar hydrogenating activity can be attained for lower n_{Pt} when a zeolite is mixed with Pt/Al₂O₃ (see Figure 2). Focusing on Pt/Al₂O₃-HUSY and Pt/Al₂O₃-HBEA catalysts, a unique evolution on the activity as function of n_{Pt} seems to occur, irrespectively of the zeolite (see Figure 2). This means that a constant TOF_{Pt} is obtain for Pt/Al₂O₃ mixed with zeolite which is independent of the $n_{Pt}/(n_{Pt}+n_A)$, contrarily to the results for Pt/zeolite catalysts.

Based on these results, it seems that, when the zeolite is separated from the hydrogenating function (Pt/Al₂O₃), the maximum enhancement of the hydrogenating activity can be achieved for lower $n_{Pt}/(n_{Pt}+n_A)$ ratios. This is an indication that only a part of the acid sites is playing a role, due to the longer H_{sp} diffusion pathway, which can be corroborated by the activities per adsorbing site. Those activities are 1.2 to 5 times lower than those of Pt/zeolite catalysts, at similar hydrogenating to adsorbing sites ratio (see Figure 1). The thermodynamics of H_{sp} diffusion may also amplify the role of inter-site distance: an intrinsic lower H_{sp} diffusion rate on Al₂O₃ can be expected comparing to that in zeolites.

The diffusion of H_{sp} on insulating materials, like Al_2O_3 and zeolites, is only possible if the support has defects [17]. However, in the case of zeolites, the presence of surface hydroxyls facilitate the surface migration of activated hydrogen [18].

As the key parameter limiting hydrogenating activity is Pt-acid site intimacy, which does not depend on the zeolite, HUSY and HBEA have a similar contribution to activity, despite their different textural and acidic properties. Furthermore, in such conditions, one may presume that only those acid sites which are near the interface of zeolite with Pt particles have an important contribution, due to its reduced Pt-acid site distance, as proposed before in literature [10].

4 Conclusion

Toluene hydrogenation was studied over catalysts based on Pt/ Al_2O_3 mechanically mixed or not with either HUSY or HBEA zeolites.

The turnover frequency of platinum is significantly higher for intimate mixtures of zeolites with Pt/ Al_2O_3 comparing to Pt/ Al_2O_3 individual catalyst. This improved activity per metal site was proposed to be caused by the hydrogenation of reactant that is adsorbed on these additional acidic sites through spilled over hydrogen (H_{sp}).

The mixture of either HBEA or HUSY zeolites with Pt/ Al_2O_3 showed a unique evolution on the activity with n_{Pt} and so a similar contribution of both zeolites to hydrogenating activity. Therefore, for a fixed Pt-acid site distance, the relevance of textural and acidic properties is low when the acid sites contribution is limited by the H_{sp} supply rate.

Comparing to Pt/zeolite impregnated catalysts, the activity per adsorbing site is lower when the Pt is deposited on Al_2O_3 , for a same metal to adsorbing sites ratio. This is proposed to be due to a detrimental effect of longer Pt-acid site distances on the rate of H_{sp} with which acid sites of zeolites are supplied.

In summary, the hydrogenating activity of zeolite-based Pt catalysts seems to be mostly a function of the accessible metal atoms, the total acid sites and the distance between Pt

clusters and acid sites. In particular, the contribution of acid sites decreases with increased Pt-acid site distances. Therefore, the toluene hydrogenation is specially fitted to establish the degree of intimacy of bifunctional catalysts.

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Figure Captions

Figure 1: Activity per total adsorbing sites as function of $n_{\text{Pt}}/(n_{\text{Pt}}+n_{\text{A}})$ for HBEA (◆) and HUSY (■) zeolites mixed with Pt/Al₂O₃ in toluene hydrogenation. Pt/HUSY (●) and Pt/HBEA (▲) series were published elsewhere [14].

Figure 2: Catalytic activity as function of accessible Pt sites for Pt/Al₂O₃-HBEA (◆), Pt/Al₂O₃-HUSY (■) and Pt/Al₂O₃ (●) catalysts in toluene hydrogenation.