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Synthesis of cyclohexylcyclohexanone on bifunctional Pd faujasites Influence of the balance between the acidity and the metallic function

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Abstract

The transformation of cyclohexanone was carried out on a series of bifunctional PdHFAU catalysts with Pd contents between 0.1 and 0.5 wt.% and framework Si/Al ratios equal to 5, 20, 40 and 100, under the following conditions: flow reactor, 473 K, pressures of cyclohexanone and hydrogen equal to 0.17 and 0.83 bar, respectively. With all the catalysts, cyclohexylcyclohexanone, the formation of which requires successive steps of aldolization, dehydration and hydrogenation, is directly formed. The effect of the balance between the hydrogenating and acid functions of the catalysts (taken as the ratio between their activity for toluene hydrogenation and their number of protonic acid sites, A_H/B) on their activity, stability and selectivity is the one expected from a bifunctional catalytic process. The activity per protonic site first increases with A_H/B, then remains constant above a certain value of A_H/B ($0.4\,h^{-1}$), the limiting step of cyclohexylcyclohexanone formation being then cyclohexanone aldolization. The selectivity to cyclohexylcyclohexanone as well as the stability increase with A_H/B remaining constant for $A_H/B > 1\,h^{-1}$. While a high selectivity to cyclohexylcyclohexanone is obtained, the catalyst stability is relatively poor due to the retention inside the zeolite micropores of polar tricyclic C_{18} compounds.

Keywords: Cyclohexylcyclohexanone synthesis; Bifunctional catalysis; PdHFAU catalysts; Activity; Stability; Selectivity

1. Introduction

Bifunctional noble metal/zeolite catalysts are mainly used in industrial processes of refining and petrochemicals [1,2]: hydroisomerization of C_5–C_6 alkanes, hydrocracking, dewaxing, isomerization of the C_8 aromatic cut. However, these catalysts could allow the "green" synthesis in one apparent step of functional compounds [3,4] whose formation requires successive steps catalyzed by acid or metallic sites and which, at the present time, is carried out in several steps over monofunctional catalysts. Indeed, these latter processes are very polluting because of the separation steps which are required and also because of the formation of a large amount of salts due to the frequent use of acid solutions as catalysts [3,5,6]. An important example of the one-step preparation of functional compounds is the synthesis of ketones such as methylisobutylketone from acetone, cyclohexylcyclohexanone (CHCHO) from cyclohexanone, 1,3-diphenylbutan-1-one from acetophenone, etc. These three ketones have various applications as solvents, fragrances, etc. [5,7–9]. Three steps are involved in their synthesis: aldolization with formation of a keto alcohol and dehydration catalyzed by acids

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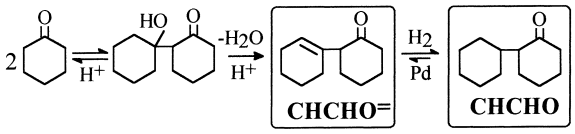
and hydrogenation catalyzed by metals. It has been demonstrated that the synthesis of these three ketones could be carried out in one apparent step over Pt or Pd zeolites [6,7,10–15]. However, the characteristics of optimal catalysts remain to be specified.

The activity, stability and selectivity of bifunctional zeolite catalysts depend on many parameters, in particular:

1. the nature of the metal (Pt or Pd),
2. the balance between the hydrogenating and the acid functions,
3. the zeolite pore structure.

This work deals with the selective synthesis of CHCHO from cyclohexanone over PdHFAU zeolites. Pd was chosen because the ratio between the rates of hydrogenation of C=C and C=O double bonds is much higher than with Pt, which limits the secondary transformations of cyclohexanone and CHCHO [13]. Furthermore, tridirectional large pore zeolites such as HFAU which allow an easy desorption of the relatively bulky product molecules have to be chosen as acid components. The objective of this work is to determine the influence of the second parameter, i.e. the balance between the hydrogenating and the acid functions.

The reaction scheme of cyclohexanone transformation was previously established over PtHMFI and PdHFAU catalysts [12,14]. Over a 0.3PdHFAU40 catalyst (0.3 wt.% Pd, framework Si/Al ratio of the zeolite equal to 40), CHCHO which results from the bifunctional three-step pathway represented in Eq. (1) appeared as a primary product.



(1)

The keto alcohol was not observed in the reaction products, which suggests its rapid dehydration on the acid sites. On the other hand, a small amount of cyclohexenylcyclohexanone ($CHCHO^{=}$) was found in the products. Various other secondary products were observed: cyclohexene, cyclohexane, methylcyclopentane and benzene (C_6), tricyclic C_{18} compounds ($TriC_6$), bicyclic C_{12} alcohols and ketones (BenzoCHO), and bicyclic hydrocarbons (BiC_6). The formation of these secondary products is described in Eqs. (2)–(5) (Scheme 1). It should be remarked that no alcohol, intermediates in Eqs. (2), (3) and (5), were observed, which confirms that alcohol dehydration is very fast.

2. Experimental

2.1. Catalysts

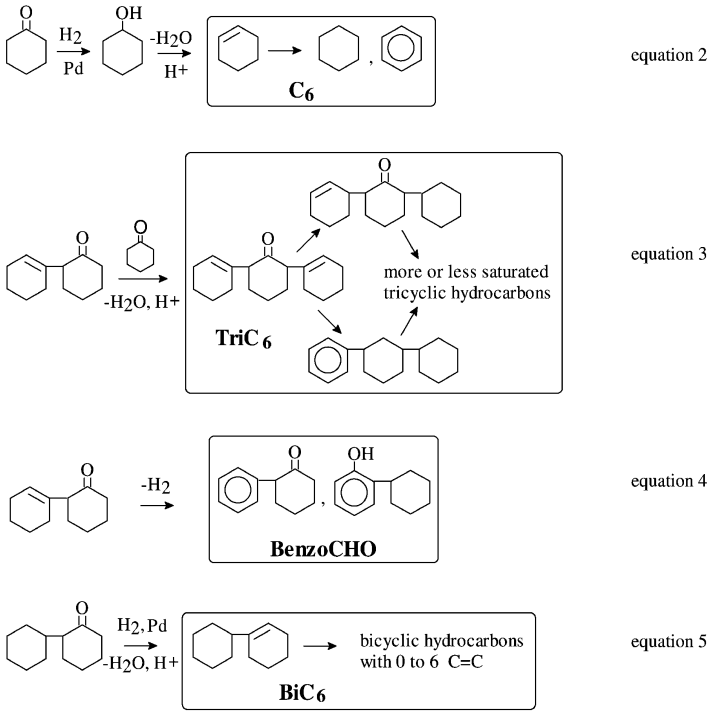
Seven *x*PdHFAU*y* samples with palladium contents (*x*) ranging from 0.1 to 0.5 wt.% and framework Si/Al ratios (*y*) of 5, 20, 40 and 100 were used in this work. The HFAU samples (CBV500, CBV720, CB780 and CBV760) were supplied by PQ zeolites and their characteristics were previously reported [16,17]. The bifunctional catalysts were prepared by ion exchange with $Pd(NH_3)_4Cl_2$ followed by calcination (6 h) under dry air flow at 573 K and reduction under hydrogen at 773 K for 8 h. Their metallic function was characterized by toluene hydrogenation at 383 K.

The characteristics of the bifunctional catalysts are listed in Table 1. The hydrogenating activity of the PdHFAU40 samples (A_H) was proportional to their palladium content, which means that the dispersion of palladium was similar for all the samples. On the other hand, for the same palladium content, i.e. 0.2 wt.%, the A_H values depend on the zeolite, the higher activity being obtained with 0.2PdHFAU40.

The concentration of protonic acid sites was determined by adsorption of pyridine followed by IR analysis [14,16]. Values of *B* in Table 1 represent the concentration of the protonic sites which retain pyridine above 423 K.

2.2. Reaction

The transformation of cyclohexanone was carried out in a flow reactor at 473 K, atmospheric pressure, $p_{H_2}/p_{cyclohexanone}=5$ and WHSV (weight of reactant injected per weight of catalyst per hour) between 3 and 67 h^{-1}. The reaction products were condensed at the reactor outlet, then analyzed by gas chromatography using a CPSil5CB capillary column of 50 m length, 0.32 mm interior diameter and 1.2 μm internal phase. Their identification was reported in a previous paper [12].



Scheme 1.

3. Results and discussion

3.1. Activity

Fig. 1 shows the change with contact time of X_0, the initial conversion of cyclohexanone, i.e. the conversion extrapolated at time-on-stream (TOS) zero [13], over five catalysts: 0.2PdHFAU5, 0.2PdHFAU20, 0.2PdHFAU100 and 0.1PdHFAU40 and 0.2PdHFAU40. The initial activity values determined from the slopes of the curves are between 9 and 60 mmol h^{-1} g_{cat}^{-1}. They increase in the following

Table 1
Characteristics of the *x*PdHFAU*y* catalysts

Catalyst	A_H (mmol h^{-1} g^{-1})[a]	B (mmol g^{-1})[b]	A_H/B (h^{-1})
0.2PdHFAU5	0.03	0.784	0.04
0.2PdHFAU20	0.08	0.327	0.24
0.2PdHFAU100	0.08	0.217	0.37
0.1PdHFAU40	0.05	0.133	0.38
0.2PdHFAU40	0.14	0.133	1.05
0.3PdHFAU40	0.23	0.133	1.73
0.5PdHFAU40	0.31	0.133	2.33

[a] Activity for toluene hydrogenation.

[b] Concentration of Brönsted acid sites which retain pyridine above 423 K, determined by TPD of pyridine followed by IR [14,16].

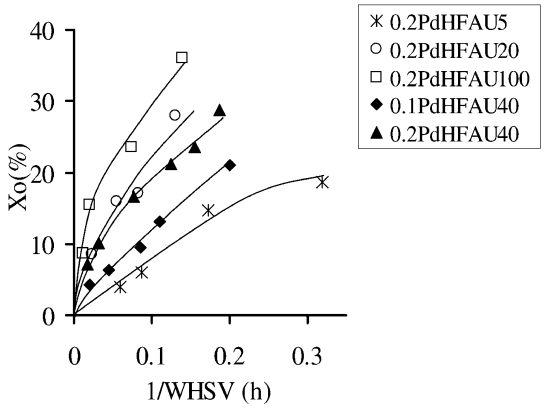


Fig. 1. Transformation of cyclohexanone over PdHFAU catalysts. Initial conversion (X_0) vs. contact time (1/WHSV).

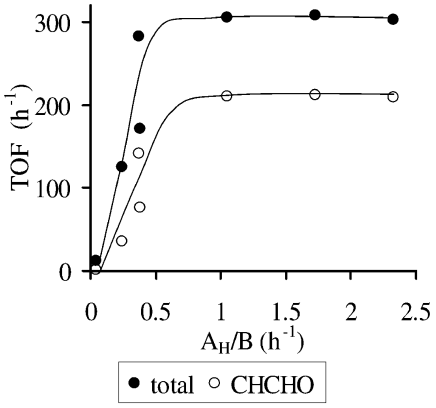


Fig. 2. Total initial activity per protonic site (TOF, total) and initial rate of cyclohexylcyclohexanone formation (TOF, CHCHO) as a function of the ratio between the hydrogenating activity and the number of protonic acid sites of the catalysts, A_H/B (h^{-1}).

order: 0.2PdHFAU5<0.1PdHFAU40<0.2PdHFAU20≈ 0.2–0.5PdHFAU40<0.2PdHFAU100. The change of the turnover frequency (TOF), i.e. the activity per protonic acid site, with the ratio between the hydrogenating activity and the concentration of protonic acid sites (A_H/B) is the one found for reactions occurring through bifunctional catalysis [1]. This could be expected since the formation of most of the reaction products (Eqs. (1)–(3) and (5)) involves steps catalyzed by acid and metallic sites. For low values of A_H/B (A_H/B lower than $0.4\,h^{-1}$), the TOF values increase with A_H/B (Fig. 2), which means that cyclohexanone transformation is limited by hydrogenation steps. For $A_H/B \geq 0.4\,h^{-1}$, the TOF value is constant, approximately 300 molecules of cyclohexanone being transformed per protonic site and per hour. Therefore, cyclohexanone transformation is then limited by acid steps. The same trend is observed for the formation of the desired cyclohexylcyclohexanone product (Fig. 2). For this reaction, the limiting step at the TOF plateau is cyclohexanone aldolization on the acid sites. Indeed, the other acid step, i.e. the dehydration of the keto alcohol is very fast [14].

3.2. Selectivity

The distribution of the products of cyclohexanone transformation calculated for an initial conversion of 30% is reported in Table 2. While this distribution depends on the catalyst, with all the samples, CHCHO is the major reaction product. The percentages of bicyclic and tricyclic compounds (BiC_6 and $TriC_6$) are practically independent of the catalyst: approximately 10% of each. On the other hand, the percentages of C_6 cyclic hydrocarbons and of bicyclic alcohols and ketones (BenzoCHO) are significant only for the catalysts with low values of A_H/B (Table 2). It should be emphasized that these C_6 and BenzoCHO compounds are the major products of cyclohexanone transformation over acid zeolite catalysts such as HFAU40 and HFAU100 [14]. Therefore, over the catalysts with low values of A_H/B, a large part of these compounds result most likely from purely acid catalyzed reactions. A high selectivity to C_6 is furthermore unexpected over palladium catalysts because of the low activity of palladium in C=O bond hydrogenation [18,19].

As expected, the CHCHO/$CHCHO^{=}$ ratio increases with A_H/B, as shown in Fig. 3a, for 30% conversion of cyclohexanone. On the other hand, the tricyclic compounds/cyclohexylcyclohexanone

Table 2
Transformation of cyclohexanone[a]

Catalyst	A_H/B (h^{-1})	Product distribution (wt.%)					
		CHCHO	$CHCHO^{=}$	C_6	BiC_6	$TriC_6$	BenzoCHO
0.2PdHFAU5	0.04	31.3	20.1	8	10.3	12	18.3
0.2PdHFAU20	0.24	45.3	10.8	7.2	13	14	9.7
0.2PdHFAU100	0.37	65	10.7	1.3	7.7	13.1	2.2
0.1PdHFAU40	0.38	63.3	8	1.5	10.7	12.8	3.7
0.2PdHFAU40	1.05	73	5	1.3	6	11.5	3.2
0.3PdHFAU40	1.73	75.7	2.7	1.6	7	9.7	3.3
0.5PdHFAU40	2.33	75.3	1	2.2	9.8	9.3	2.4

[a] Selectivities of bifunctional *x*PdHFAU*y* catalysts.

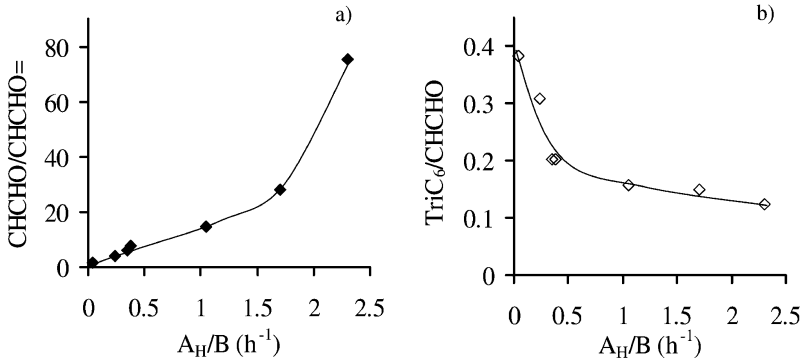


Fig. 3. Ratio at 30% cyclohexanone conversion between the selectivities to cyclohexylcyclohexanone and cyclohexenylcyclohexanone ($CHCHO/CHCHO^{=}$) (a) and to tricyclic compounds and cyclohexylcyclohexanone ($TriC_6$/CHCHO) (b) as a function of the ratio between the hydrogenating activity and the number of protonic acid sites of the catalysts, A_H/B (h^{-1}).

ratio ($TriC_6$/CHCHO) decreases when A_H/B increases (Fig. 3b). This can be explained by the competition between the hydrogenation of $CHCHO^{=}$ (Eq. (1)) and the acid addition of cyclohexanone over $CHCHO^{=}$ with formation of $TriC_6$ (Eq. (3)).

The selectivity to the desired product (CHCHO) increases first with A_H/B, then remains constant (75%) for $A_H/B \geq 1\,h^{-1}$ (Fig. 4). This is due to the fact that the decrease in $CHCHO^{=}$ and $TriC_6$ when A_H/B increases, is balanced by an increase in BiC_6. The latter increase can be explained by the secondary transformation of CHCHO into BiC_6 (Eq. (5)). The significance of this reaction would increase with A_H/B because hydrogenation of C=O is much slower than dehydration. Indeed, whatever the catalyst, no alcohol was observed indicating that dehydration is a very fast reaction. Hence, in the transformation of CHCHO into BiC_6, hydrogenation of CHCHO is the limiting step. It should, however, be emphasized that hydrogenation of substituted ketones such as CHCHO was found to be faster than hydrogenation of non-substituted ones such as cyclohexanone [20], which explains that the selectivity to BiC_6 is higher than the selectivity to C_6 (Table 2).

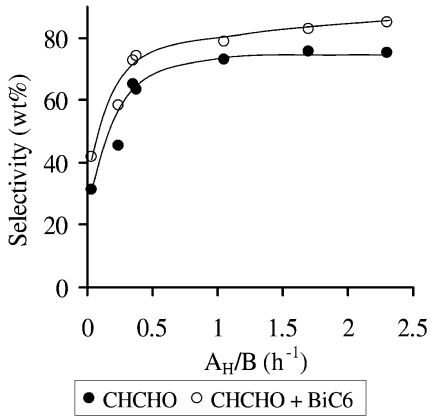


Fig. 4. Selectivities of cyclohexanone transformation (30% conversion) into cyclohexylcyclohexanone (CHCHO) and into cyclohexylcyclohexanone+bicyclic hydrocarbons ($CHCHO+BiC_6$) as a function of the ratio between the hydrogenating activity and the number of protonic sites of the catalysts, A_H/B (h^{-1}).

3.3. Stability

The residual activity of the catalysts (A_R), i.e. the ratio between the conversion at a certain TOS and X_0 the initial conversion of cyclohexanone (the contact time was chosen in order to have X_0 close to 20% with all the catalysts) decreases rapidly with TOS (Fig. 5). All the catalysts have a poor stability. However, this stability increases with A_H/B, as shown in Fig. 6, in which A_R after 300 min is plotted versus A_H/B. Fig. 6 also shows that the catalyst deactivation is due to the formation of carbonaceous deposits ("coke"): indeed, the lower the "coke" content, the higher the A_R value (Fig. 6). It should be remarked that at low A_H/B values, A_R increases with A_H/B and the "coke" content decreases, whereas for $A_H/B \geq 1\,h^{-1}$, A_R and the "coke" content are practically constant. A similar behavior

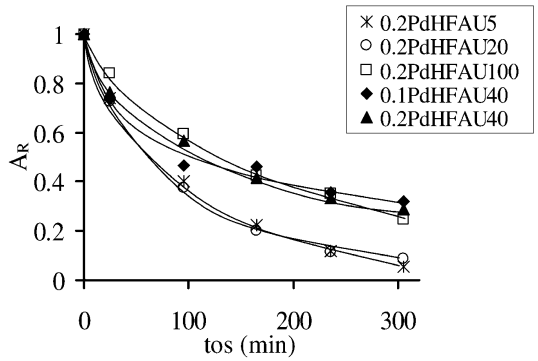


Fig. 5. Transformation of cyclohexanone over PdHFAU catalysts. Residual activity (A_R) vs. TOS.

was observed in *n*-alkane hydrocracking, but in this case, the residual activity became close to 1 (i.e. there is no deactivation) for high values of the balance between hydrogenating and acid activities [21].

Part of the carbonaceous deposits (7.5 wt.%) can be solubilized in methylene chloride by direct soxhlet treatment of the "coked" catalyst, the other part being solubilized only after dissolution of the zeolite in hydrofluoric acid [22]. Both fractions were mainly constituted by $TriC_6$ compounds with generally one oxygen atom. The kinetic diameter of the corresponding molecules being lower than the size of the HFAU micropores, their retention is mainly due to the adsorption of these polar molecules on the acid sites. The decrease in "coke" content, when A_H/B increases, can be explained by conversion of polar molecules into less polar molecules. In particular, ketonic coke components can undergo successively hydrogenation, dehydration and hydrogenation steps leading to tricyclic saturated hydrocarbons which desorb easily from the zeolite micropores.

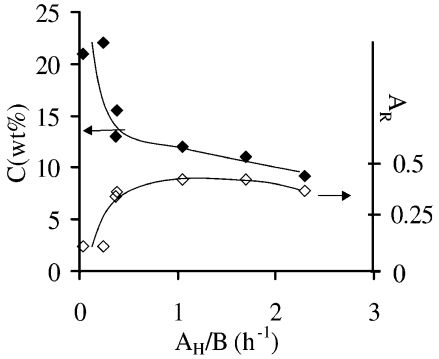


Fig. 6. "Coke" (as %C) and residual activity (A_R) at TOS=300 min as a function of the ratio between the hydrogenating activity and the number of protonic sites of the catalysts, A_H/B (h^{-1}).

4. Conclusion

The transformation of cyclohexanone into CHCHO which requires three successive steps catalyzed by acid sites (aldolization, dehydration) and metallic sites (hydrogenation) can be carried out in one apparent step over PdHFAU catalysts. The keto alcohol resulting from cyclohexanone aldolization is never observed because of its very fast dehydration on the zeolite acid sites. Only a small amount of the other intermediate ($CHCHO^{=}$) is formed with the more selective catalysts. With these catalysts, the selectivity to CHCHO is equal to 75% at 30% conversion, the main secondary products being BiC_{12} and $TriC_{18}$ hydrocarbons. The main problem with these catalysts is their relatively fast deactivation owing to the retention of tricyclic polar compounds inside the zeolite micropores. The change in the activity, stability and selectivity of the catalysts with the balance between the hydrogenating and the acid functions is the one expected from a bifunctional catalytic process.

Acknowledgements

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