

# Benzaldehyde hydrogenation over supported nickel catalysts

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## Abstract

The hydrogenation of benzaldehyde over nickel catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> and CeO<sub>2</sub> was studied at atmospheric pressure in the range temperature of 70–140 °C under H<sub>2</sub> flow. They were characterized by their BET surface area, XRD spectra, reducibility properties under H<sub>2</sub>. The obtained products were benzylalcohol, toluene, benzene with yields depending on the nature of the support and reaction temperature. Methylcyclohexane was also produced, mainly at low temperature and on Ni/α-Al<sub>2</sub>O<sub>3</sub> as catalyst. The products of benzaldehyde hydrogenation (benzylalcohol, toluene and methylcyclohexane) and hydrogenolysis (benzene) were preferentially formed at low/ middle and high reaction temperature respectively. The observed selectivities also suggested the existence of bifunctional sites for both the hydrogenation and hydrogenolysis reactions. These sites were believed to be involved as acidic/cationic centers for the adsorption of the oxygenate molecules and metal center for the hydrogenation or hydrogenolysis step.

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**Keywords:** Nickel; Catalyst; Support; Benzaldehyde; Hydrogenation

## 1. Introduction

One class of reactions important to produce fine chemical compounds is the hydrogenation of aldehydes and ketones containing unsaturated C=C bonds [1–6]. The selective hydrogenation of crotonaldehyde and butyraldehyde [7], and most recently, phenylacetaldehyde [8], benzaldehyde and *O*-tolualdehyde [9] have received a growing interest since the production of fine chemicals by selective catalytic activation of carbonyl because it is the challenge for reduction of energy consumption. It was found that nickel, platinum and copper based catalysts preferentially hydrogenate the carbonyl group [9,10–14]. For the aromatic compounds, the benzene ring and the carbonyl group should be hydrogenated but hydrogenolysis should also compete [9,15,17]. The obtained selectivities mainly depended on the nature of the catalyst [2–4,9,15].

Heterogeneous catalytic studies of benzaldehyde hydrogenation have been largely devoted to the liquid phase medium [5,6,18,19] whereas relatively few studies have been reported for the gas phase medium [9,15,16,20]. The later system were studied over Pt [15] or Ni [9] supported catalysts or metal oxides catalysts [16]. For the metal supported catalysts it was suggested that the observed performances were related to new active sites created in the metal–support interfacial region [15,21] whereas for metal oxides catalysts it was found that they strongly depended on both the reducibility and surface acid–base properties [16]. We recently confirmed the role of metal and acid–base properties in the same reaction conducted over copper supported catalysts [20].

The aim of the present paper is to report the study of the hydrogenation properties of 10% nickel catalysts impregnated on α-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub> supports: α-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are both unreducible oxides and, also, amphoteric and acidic respectively; TiO<sub>2</sub> and CeO<sub>2</sub> are reducible oxides and, in addition, behave as basic oxides [16]. The catalysts were characterized by their BET surface area, XRD spectra and reducibility under H<sub>2</sub> flow. The reaction was performed at atmospheric pressure in the reaction temperature range of 70–140 °C.

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Table 1  
Nickel supported catalysts and their properties

Catalysts	NiO/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	NiO/SiO <sub>2</sub>	NiO/TiO <sub>2</sub>	NiO/CeO <sub>2</sub>
Ni (wt.%)	9.5	8.9	9.6	9.2
Support origin	Fluka	Fluka	Merck	Labosi
Support $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	10	200	80	100
Catalyst $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	4.0	130.0	70.0	90.0
Degree of reduction (%)	85	45	80	70
$T$ (°C) of peak of reduction	480	440	450	440
	–	650	510	–
XRD Identification phases	NiO (benzenite) Al <sub>2</sub> O <sub>3</sub> (corundum)	NiO (benzenite) SiO <sub>2</sub> (amorphous)	NiO (benzenite) TiO <sub>2</sub> (rutile)	NiO (benzenite) CeO <sub>2</sub> (cerianite)
Crystallite size <sup>a</sup> (nm)	12	22.4	10.1	14.4
Degree of dispersion (%)	7.5	4.02	8.91	6.25
Metallic surface area (m <sup>2</sup> g <sup>-1</sup> )	3.28	1.65	3.94	2.65

<sup>a</sup> Determined after calcination step by XR Diffraction using Debby-Scherrer equation.

## 2. Experimental

### 2.1. Catalysts preparation and characterization

The catalysts were prepared by impregnation of an aqueous suspension of the support by nickel nitrate, then evaporating the solvent at 80 °C and drying at the same temperature for 12 h. The obtained precursors were calcined at 350 °C in air for 3 h. All the supports were commercial materials (Table 1) and calcined before impregnation in air at 500 °C for 2 h.

The contents of nickel were determined by atomic absorption. The specific area measurements were performed by the classical BET method on a Coultronics 2100E apparatus. The data were interpreted using the BET equation and an effective cross-sectional area of 16.2 Å for N<sub>2</sub>. The measurement was then made at liquid nitrogen temperature (196 °C) with nitrogen as adsorbate.

Identification of crystalline compounds and determination of average crystallite size were carried out by X-ray diffraction (XRD) using Phillips PN-1710 diffractometer with Ni filter and Cu K $\alpha$  monochromatic radiation. The average size of the metal particle was calculated from the linewidth at half height of the NiO peaks using the Scherrer equation with Warren's correction for instrumental line broadening [22]. The determination of particle size of nickel was used to calculate the dispersion and the metal surface area of nickel assuming that metallic nickel forms spherical particles.

The reducibility experiments were carried out on a pulse chromatographic reactor. The sample (0.1 g) was dried at 150 °C for 2 h in argon (99.95%, Air Liquide) and then cooled to room temperature under argon flow. The flow was then switched to hydrogen (99.995%, Air Liquide) and the sample heated up to 650 °C at a rate of 4 °C min<sup>-1</sup>. The degree of reduction of nickel was calculated assuming its oxidation state was +2 after calcination.

### 2.2. Catalytic testings

The catalytic performances were carried out in a fixed-bed glass tubular reactor with 0.2 g samples at atmospheric pressure and the total flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. The reactant gas

feed consisted of 4.8 Torr of benzaldehyde (Aldrich, 99.98%) and 250 Torr of H<sub>2</sub> diluted in N<sub>2</sub>. Gaseous benzaldehyde was obtained by bubbling N<sub>2</sub> in liquid benzaldehyde maintained at constant temperature (50 °C) in a suitable saturator. Before testing, the catalysts were in-situ reduced for 16 h at 350 °C in a current of H<sub>2</sub> with a flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>.

The gaseous reactant and products were heated upstream and outstream and analyzed on line by a FID gas chromatograph (Delsi IGC 121 ML) equipped with a 10% CP-SIL 8 CB/ Chromosorb W column. Each reaction temperature was maintained constant until the corresponding steady-state was reached as indicated by the gas chromatograph analysis of the exit gases samples. For each catalyst the reaction temperature was changed in a crossing order: 110 °C, 140 °C, 70 °C. Varying the flow rate and sample weigh in the range 10–80 cm min<sup>-1</sup> showed that no mass transfer limitations occurred when the sample weight was  $\leq 0.2$  g.

## 3. Results and discussion

### 3.1. Catalysts characterization

The specific area of the catalysts increased with that of the corresponding supports and were in the range 4–127 m<sup>2</sup> g<sup>-1</sup> (Table 1). However, this range of specific area is lower than that of the supports (10–200 m<sup>2</sup> g<sup>-1</sup>). During the impregnation stage of the preparation, surface hydroxyl groups of the support were consumed by reaction with the active phase precursor. Such a surface reaction may have caused the decrease of available surface area of the support, probably by closure of the pores.

In other respects, the XRD spectra showed the characteristic bands of the nickel phase and support but no mixed nickel oxide-support phases was identified. The pattern for the supports was that of crystallized materials with well-defined bands except for the amorphous SiO<sub>2</sub> support. The pattern Ni (200) XRD lines of nearly the same width dominate the spectra of every sample. The metal phase was of 'CFC' structure for all the catalysts. Calculations showed that the mean crystallite size of nickel was not the same for all the catalysts, and vary in the range 10.1–22.4 nm (Table 1). The crystallite size had essential effect on the dispersion and surface area of nickel. The results

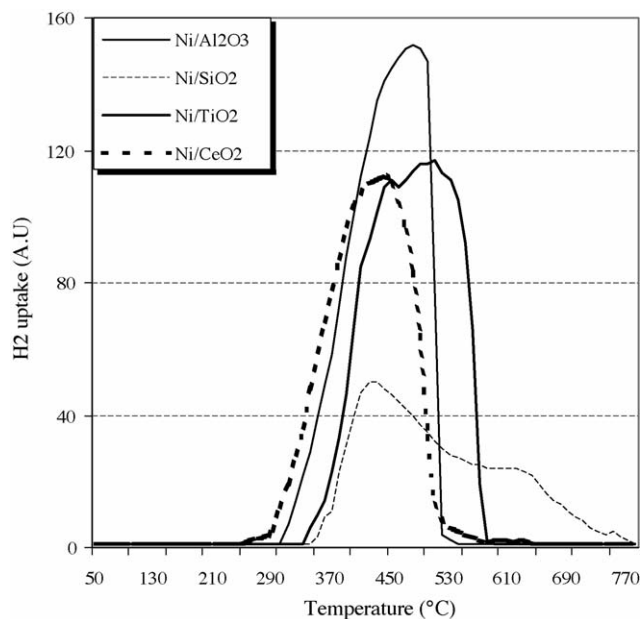


Fig. 1. TPR profile of various supported nickel oxide catalysts.

showed that the dispersion of nickel increased with metallic surface area, whereas the crystallite size decreased.

In general, the interaction of metal is stronger with  $\text{TiO}_2$  ( $6.4 \text{ m}^2_{\text{Ni}} \text{ g}^{-1}_{\text{cat}}$ ) than with  $\text{SiO}_2$  ( $2.7 \text{ m}^2_{\text{Ni}} \text{ g}^{-1}_{\text{cat}}$ ). The strong interaction between the metal and the support results in high dispersion and small changes in the metal particle distribution during the reduction.

Under  $\text{H}_2$  atmosphere the supported NiO phase was reduced in one (Ni/ $\text{Al}_2\text{O}_3$  and Ni/ $\text{CeO}_2$ ) or two steps (Ni/ $\text{TiO}_2$  and Ni/ $\text{SiO}_2$ ) as shown in Fig. 1. The reduction was incomplete (45–85%) (Table 1). Fig. 1 shows that the peaks are broad and indicates that a broad range of metal–support interaction occur in these samples with the possibility of the nickel particles size distribution playing an important role during the reduction. The strong metal–support interaction has been reported to be manifested as a different particle shape when such an interaction occurs between metal and oxide [23,24]. In connection, the existence of two peaks of reduction would indicate two type of metal particles or two main domains of metal–support interaction. The peaks appeared between 450 and 510 °C over all catalysts may be attributed to Ni particles dispersed on the surface and bulk. In such a case,  $\text{H}_2$  consumption at temperature higher than 510 °C may be attributed to the reduction of large Ni particles or in strong interaction with the support. The small peak at 450 °C (Ni/ $\text{TiO}_2$ ) could be assigned to a reduction of dispersed Ni in isolated patches. The reduction peak temperature of Ni/ $\text{SiO}_2$  (650 °C) are higher than those of the other supported catalysts, suggesting the occurrence of a presence of a bigger nickel particles on  $\text{SiO}_2$  support.

### 3.2. Benzaldehyde hydrogenation

#### 3.2.1. Catalytic activity

The bare oxides were almost all inactive in benzaldehyde hydrogenation in the whole range of reaction temperature. Much

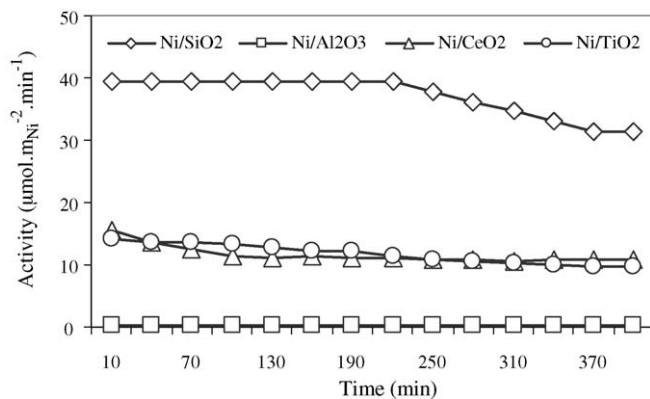
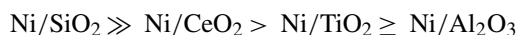


Fig. 2. Activity rate with time on stream in benzaldehyde hydrogenation over the Ni supported catalysts at 70 °C.

higher activities were obtained in the presence of nickel, indicating that the latter was the main component of the active site.

At the low reaction temperature (70 °C), the nickel catalysts exhibited initial deactivation before the steady-state was established and the degree of deactivation depended on the nature of the support. Fig. 2 reports activity results with time on stream at 70 °C. It can be noted in this figure that Ni/ $\text{Al}_2\text{O}_3$  was the less active whereas Ni/ $\text{SiO}_2$  was the most active that exhibits little deactivation with time on stream. On Ni/ $\text{CeO}_2$  and Ni/ $\text{TiO}_2$  catalysts, a drop of activity from 18.4 to  $10.4 \mu\text{mol m}_{\text{Ni}}^{-2} \text{ min}^{-1}$  and 16.4 to  $9.8 \mu\text{mol m}_{\text{Ni}}^{-2} \text{ min}^{-1}$ , respectively was observed after about 6 h working (Table 2). At 110 and 140 °C of reaction temperatures, the initial activity rate was maintained with time on stream and no deactivation was observed for all catalysts (Table 2). In any case, the deactivation was reversible since the activity was almost totally recovered after increasing the reaction temperature. The decrease of activity is attributable to the catalyst poisoning by strongly adsorbed oxygenate molecules [20].

The initial activity rate with the reaction temperature for all catalysts (Table 2) showed that the level and order of activity depended on both the reaction temperature and nature of the support. At the reaction temperatures of 110 and 140 °C the Ni/ $\text{SiO}_2$  catalyst was by far the most active and the order of activity was as follows:



Such an order seems to be related to the crystallite size of the nickel phase (see Table 1). Indeed, the weak activity of NiO on  $\text{Al}_2\text{O}_3$  support is probably due to the presence of small crystallites of nickel in strong interaction with the support. The formation of small crystallites to be related to the high dispersion and to the high metallic surface area of nickel on the alumina support (Table 1). Inversely, the low metallic surface area of nickel on the silica support encouraged the NiO crystallites formation of the order of 22 nm. The probably presence of weak interaction between metal–support due to the little dispersion of nickel entailed the formation of the thick particles. What probably contributed to the increase of the catalytic activity.

Then, as above mentioned, the explanation of the weak activity in the hydrogenation of carbonyl bonds observed for the

Table 2  
Catalytic results for benzaldehyde hydrogenation over Ni supported catalysts

Catalysts	$T$ (°C)	$W_0$ ( $\mu\text{mol m}^2_{\text{Ni}} \text{min}^{-1}$ ) <sup>a</sup>	$W^b$ ( $\mu\text{mol m}^2_{\text{Ni}} \text{min}^{-1}$ )	Selectivity <sup>b</sup> (%)							
				BOL		TOL		MECH		BENZ	
Ni/Al <sub>2</sub> O <sub>3</sub>	70	0.43	0.32	– <sup>c</sup>	– <sup>b</sup>	40 <sup>c</sup>	– <sup>b</sup>	16 <sup>c</sup>	70 <sup>b</sup>	44 <sup>c</sup>	30 <sup>b</sup>
	110	9.52	9.08	13 <sup>b</sup>	39	52	28	–	–	35	33
	140	16.23	16.10	21	15	34	38	–	–	45	47
Ni/SiO <sub>2</sub>	70	36.25	35.46	21	30	75	63	–	5	12	2
	110	40.19	40.19	–	–	87	58	–	10	13	5
	140	40.19	40.19	–	–	75	70	–	8	25	22
Ni/TiO <sub>2</sub>	70	14.57	9.77	–	90	80	4	–	–	40	6
	110	15.63	15.63	20	37	52	36	–	–	28	27
	140	16.35	16.17	25	5	50	64	–	–	35	31
Ni/CeO <sub>2</sub>	70	18.39	10.53	20	27	56	53	–	–	24	20
	110	24.45	24.45	–	–	76	77	–	3	24	20
	140	24.45	24.45	–	–	75	75	–	4	35	21

BOL: benzylalcohol, TOL: toluene, MECH: methylcyclohexane, BENZ: benzene.

<sup>a</sup> Initial rate,  $W_0$ : measured from the conversion–contact time dependencies and extrapolated to zero conversion.

<sup>b</sup> Steady-state activity and selectivity measured after 6 h of reaction time.

<sup>c</sup> Initial selectivity measured from the conversion–contact time dependencies and extrapolated to zero conversion.

Ni/Al<sub>2</sub>O<sub>3</sub> catalyst may reside in the existence of special sites formed by metal–support interaction, probably composed of at least one metal adjacent to a defect site on the support, such as Al<sup>3+</sup> cation. This allows a strong interaction between the multicentred site and the highly polarized C=O double bond of the carbonyl compound [25,26].

In addition, strikingly, a gap of initial activity was observed between 70 and 110 °C in the case of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, the reaction rate of which was multiplied by 24 (Table 2). In the same range of temperature, the gap is only of 1.3 for Ni/CeO<sub>2</sub> and almost no change is observed in the whole range of reaction temperature for Ni/SiO<sub>2</sub> and Ni/TiO<sub>2</sub> catalysts.

A similar observation has been already reported by our group in the case of the hydrogenation of benzaldehyde over copper supported catalysts [20]. We suggested that, besides reducibility properties, acid–base properties of the catalysts would also be involved. Also, for the present alumina supported nickel catalyst, intermediate oxygenated surface species formed and strongly held on these sites, should have acted as inhibiting entities, maintaining low activity in the low reaction temperature domain. At higher reaction temperature these species readily decomposed whereas the metallic nickel sites became more active, thus explaining the important gap observed in activity rate (Table 2).

On Ni/CeO<sub>2</sub> and Ni/TiO<sub>2</sub> catalysts, the oxygenate intermediates were also bounded but probably less firmly. For these supports metal–support interaction would have played an important role as well. For the most active catalyst Ni/SiO<sub>2</sub>, the probably presence of weak metal–support interaction could be to the origin of the thick nickel particles formation, therefore to the little dispersion of nickel on the support. Besides, probably no or little base sites on SiO<sub>2</sub> support were available for adsorption of the reactant or product molecules; then no inhibition of the reaction course and, consequently, no important activity change was detected with the change of the reaction temperature.

Adsorption studies of benzaldehyde over several metal oxides [27] strengthens the hypothesis of the contribution of the acid–base properties of the SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> supports. Indeed, an IRTF study [27] showed that the adsorption of benzaldehyde on silica occurs through a hydrogen bond of the oxygen atom of the C=O group to the surface silanol groups whereas for the rather basic alumina it involves a nucleophilic attack at the carbonyl center by surface oxygen (or hydroxyl), producing surface benzoate species [28]. Moreover, stable surface oxygenated intermediates have also been detected in the hydrogenation of CO on nickel-based catalysts [29]. They were identified as methoxy species on the alumina support but not found on the silica support [30–33].

### 3.2.2. Selectivity

The reaction products were benzyl alcohol, toluene, methylcyclohexane and benzene (Table 2). They resulted from three types of reaction:

- (i) C=O double bond reduction to benzyl alcohol, toluene and methylcyclohexane;
- (ii) Reduction of the aromatic ring to methylcyclohexane;
- (iii) C–C exocyclic bond hydrogenolysis to benzene.

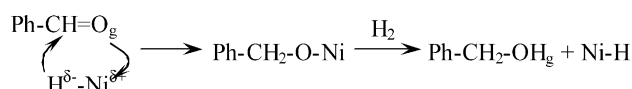
**3.2.2.1. C=O double bond reduction.** The reduction of the carbonyl function was observed at rather low temperature with high selectivity, regardless of the activity level (Table 2). For example, at 70 °C, the C=O reduction selectivity and activity were in the range 70–100% and 0.3–36.3  $\mu\text{mol m}_{\text{Ni}}^{-2} \text{min}^{-1}$  respectively. At 140 °C the C=O reduction selectivity decreased down to 40–80% whereas the activity increased to 16.1–40.2  $\mu\text{mol m}_{\text{Ni}}^{-2} \text{min}^{-1}$ . The correlation between these results and reducibility properties was not obvious because of the multiplicity of the involved chemical processes (reduction of the C=O double bond or aromatic ring,

hydrogenolysis of the external C–C bond). Also we discuss below the individual selectivities.

**Benzylalcohol selectivity.** As a general trend, benzylalcohol appeared as a low reaction temperature product (70 °C) rather favored on Ni/CeO<sub>2</sub> and Ni/SiO<sub>2</sub> (20–30% of selectivity) and in the whole range of reaction temperature on Ni/TiO<sub>2</sub> (5–90%) (Table 2). The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst did not form the alcohol product at this temperature but only from above 110 °C (10–40% of selectivity) as a consequence of adsorption phenomena, as discussed above.

The analysis of the results revealed that the high benzylalcohol selectivities appeared on the least active catalysts Ni/TiO<sub>2</sub> (90% at 70 °C) and Ni/Al<sub>2</sub>O<sub>3</sub> (39% at 110 °C). A strong metal–support interaction and high dispersion of nickel on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports would have played an important role. A small nickel particle formation may contributed to the high benzylalcohol selectivity.

The chemical process of benzylalcohol formation is believed to be a 1–2 nucleophilic addition, with a high polarization of the transition state, as in the case of the hydrogenation of conjugated carbonyl compounds [1,10,11,21]:



As reported above, the reaction needs centers for both the activation and reduction of the carbonyl function, that is specific sites would be involved, probably at the metal–support interfacial region [11–13,34,35,36–38]. The proposal that special sites are created at the metal–support interface was first made by Burch and Flambard for Ni/TiO<sub>2</sub> [34]. The active sites were suggested to consist of a special ensemble composed of at least one metal cation adjacent to a defect site on the support [34,39]. Such a configuration is believed to allow a chemical interaction between the oxygen atom in the carbonyl bond and the support thereby polarizing and activating the C=O bond [21] towards hydrogen. Similar models were subsequently utilized for other metals such as Cu [20,35], Pt [39], Pd [40,41] and Rh [42,43]. It is worth to note that they were also used for CO hydrogenation, e.g., for Pt/CeO<sub>2</sub> catalysts [44]. In this case the presence of anion vacancies at the metal–support interface was associated with the capability to facilitate CO dissociation and allow insertion mechanism to produce higher alcohols [45]. In this concept, one could anticipate that carbonyl bonds would be activated by acid surface properties.

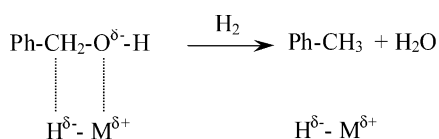
**Toluene selectivity.** Toluene appeared as a product of moderate reaction temperature (110 °C). It is favored on Ni/CeO<sub>2</sub>, Ni/TiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts (70–90% of selectivity) (Table 2). The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was the less active in this reaction (25–40% of selectivity only). A close inspection of these selectivities showed no special trends, because of the intervention of complex factors governing the mechanisms of both formation and chemical transformation of toluene.

The results regrouped in Table 2 show that, in the whole domain of the reaction temperature, toluene appears since the start of the reaction. After 6 h in the reaction, we noted that, at

70 °C, the toluene selectivity decreases with the increasing of the alcohol selectivity.

Inversely, at 140 °C, the benzylalcohol selectivity decreased on Ni/TiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with the increasing of the toluene selectivity. This result proves that the alcohol is a product of low reaction temperature and confirms that toluene is produced directly by benzylalcohol.

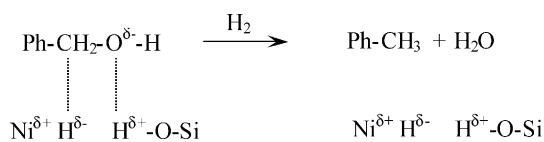
Now, it is well established that toluene is the product of the consecutive reaction of benzylalcohol hydrogenolysis [9,15,16,20,46,47]. In a parallel experiment, replacing benzaldehyde by benzylalcohol in the reactant flow showed the formation of toluene with a selectivity of 100%. In the allylalcohol hydrogenolysis on copper chromite catalysts, it is admitted that toluene would be formed on a complex site involving the oxide support rather than the copper phase [11,12]. The complex site would be bifunctional in nature, implying the metal cation and hydride entities interacted with the oxygen and carbon atoms of the alcohol molecule respectively



By analogy, we propose a similar mechanism of benzylalcohol hydrogenolysis to toluene on nickel catalysts. This mechanism may hold for the catalysts supported on TiO<sub>2</sub> and CeO<sub>2</sub> reducible oxides which are more prone to form metal hydride species and possess Ti<sup>3+</sup> or Ce<sup>3+</sup> metal cation sites. Also, it probably holds for Ni/Al<sub>2</sub>O<sub>3</sub> which is known to favor the formation of occluded hydrogen species when associated with transition metals [48,49]. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst has been also shown to enhance methanation activity in CO hydrogenation [29–31,50,51] and it was suggested that support-bound methoxy species may be responsible for the higher methanation activity. Furthermore, isotopic labeling experiments implied that the methoxy group was hydrogenated directly to CH<sub>4</sub> without first decomposing [51]. Also, in benzaldehyde hydrogenation over Ni/Al<sub>2</sub>O<sub>3</sub>, the carbonyl compound coordinated with an Al<sup>3+</sup> cation could be a precursor of the alkoxy species which can react with hydrogen spilled over from the metal surface.

In such a case, the activity in toluene should reflect the aptitude of the reduced support oxide to both adsorb the alcohol through acid–base property and dissociate H<sub>2</sub> through metal property.

In the case of the Ni/SiO<sub>2</sub> catalyst, we have reported above that benzaldehyde adsorption resulted in the interaction between its oxygen atom and the hydrogen atom of the silanol groups [27]. Also, one is allowed to think that toluene formation is probably resulted in the protonation of the alcohol function on a silanol Brönsted acid site (H–O–Si) followed by the hydrogenolysis of the protonated species on an adjacent nickel site:



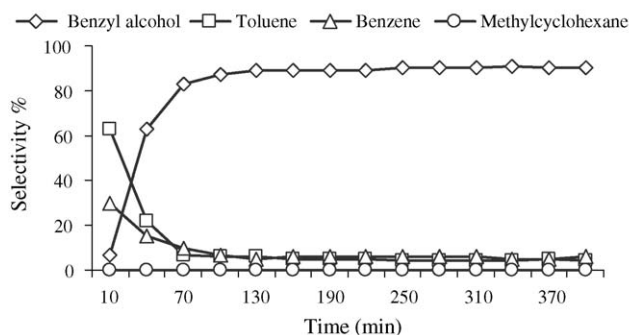
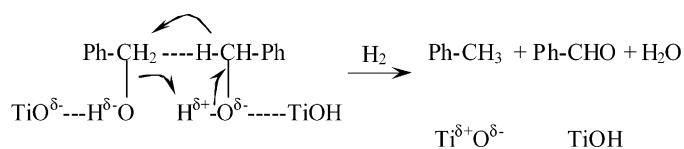


Fig. 3. Selectivity with time in benzaldehyde hydrogenation at 70 °C for the Ni/TiO<sub>2</sub> catalyst.

It is worth to note that, during the steady-state setting-up of Ni/TiO<sub>2</sub> at 70 °C, toluene appeared as a secondary product (Fig. 3). The formation of toluene as secondary product and at a so low reaction temperature, suggests the existence of another reaction path than that described above. This path probably involves very active sites on which toluene is fastly formed in the early stages of the reaction where the partial pressure of both reactants and products were low. These sites were then poisoned at higher conversion by the one or the other reactant molecule, even water. The possible route would be the benzylalcohol dismutation to toluene, benzaldehyde and water on the support [51–53]:



The reaction probably proceeds through hydride transfer between two adsorbed benzylalcohol molecules over specific acid–base sites of the support [51,52]. These sites would be poisoned with time on stream. Such a mechanism was reported for benzylalcohol dismutation to toluene over alumina catalyst [52]. This catalyst was shown to deactivate by prolonged usage or by water addition [52].

**3.2.2.2. Methylcyclohexane selectivity.** Methylcyclohexane appeared as a product of low reaction temperature (70 °C), mainly with Ni/Al<sub>2</sub>O<sub>3</sub> (70% of selectivity) as shown in Table 2. It was formed at steady-state to a smaller extent with the other catalysts : about 10% of maximum of selectivity at 110 °C for Ni/SiO<sub>2</sub> and traces for Ni/CeO<sub>2</sub>. Interestingly, during the steady-state setting-up, methylcyclohexane selectivity increased with time on stream whereas that of toluene decreased (Table 2). The phenomena was particularly clearly observed for the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at the reaction temperature of 70 °C (Fig. 4). These trends strongly suggest that toluene was the reaction intermediate to methylcyclohexane. In the case of Ni/Al<sub>2</sub>O<sub>3</sub>, the absence of benzylalcohol or toluene in the gas phase at steady-state suggests that they were strongly bounded to the surface through their oxygen atom or aromatic ring respectively at low reaction temperature. At higher reaction temperature, because less bounded to the surface, these

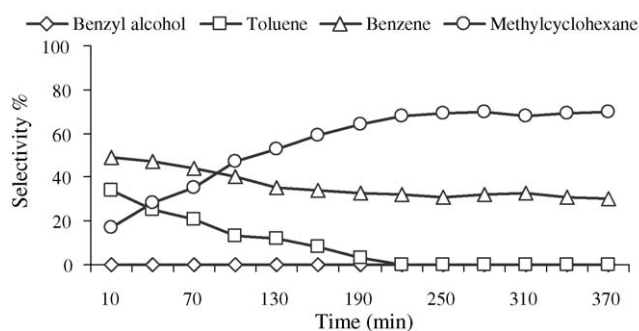
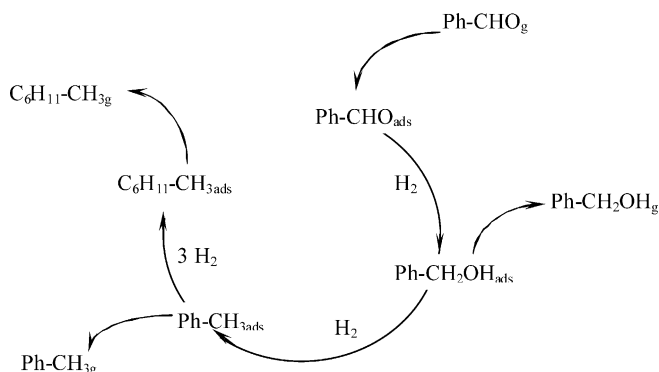
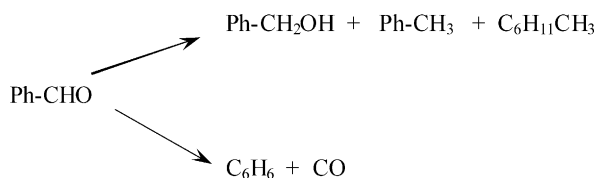


Fig. 4. Selectivity with time in benzaldehyde hydrogenation at 70 °C for the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

compounds were more easily desorbed and then produced in the gas phase at the expense of methylcyclohexane. In the case of the other catalysts, methylcyclohexane formation competed with that of the other reduction products with amounts varying with the nature of the support or reaction temperature. We can conclude that the mechanism of benzaldehyde reduction proceeded through a rattle mechanism:



**3.2.2.3. Benzene selectivity.** Benzene was formed at rather high reaction temperature (20–80%), preferentially on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 2). No cyclohexane was detected indicating a high stability of benzene in the reaction conditions used, even at low reaction temperature with the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The production of methylcyclohexane and not of cyclohexane may simply be due to the higher reactivity of toluene as compared to that of benzene. On the other hand, the study of the activity as a function of time on stream showed that benzene also arose as a primary product (Fig. 4). This result significantly shows that benzene was formed by an independent way from that of the products of benzaldehyde reduction:



This mechanism is in good agreement with the published kinetics data on benzaldehyde hydrogenation over supported nickel catalyst [9] showing that benzene was directly produced from the reactant molecule and not from the alcohol or toluene inter-

mediates. The same reaction scheme was proposed with other catalytic systems [9,20]. Carbon monoxide was identified as co-product of benzene [15].

The exact nature of the reaction paths of benzaldehyde hydrogenolysis to benzene and carbon monoxide is not yet reported to the best of our knowledge. It probably implies a bifunctional site: the adsorption of the reactant molecule on an acidic/cationic site then dissociation of the aldehydic C–H bond on a metal site. Further work is needed to obtain more information on the real involved reaction paths.

#### 4. Conclusions

The hydrogenation of benzaldehyde over nickel catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> and CeO<sub>2</sub> at atmospheric pressure and 70–140 °C produced competitively benzylalcohol, toluene, benzene and methylcyclohexane with yields depending on the nature of the support and the reaction temperature. The order of activity was attributed to crystallite size and degree of dispersion of nickel on the supports. The acid–base properties can operate and induced adsorption phenomena which explained a gap in activity between 70 and 110 °C, notably for Ni/Al<sub>2</sub>O<sub>3</sub> for which the activity was multiplied by 24: the lower the reaction temperature the stronger held were the benzaldehyde or benzylalcohol molecules the stronger was the inhibiting effect of the support on the reaction course; conversely, the higher the reaction temperature the lower the adsorption effect the higher activity rate. On the other hand, the obtained results suggested the existence of bifunctional sites both for the transformation of benzaldehyde through hydrogenation to benzylalcohol, toluene or methylcyclohexane and hydrogenolysis to benzene. These sites involved an acidic/cationic center for the adsorption of the oxygenate molecules and a metal center for the hydrogenation or hydrogenolysis step.

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