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Preparation and characterization of X wt-%Ru/Al_2O_3 catalysts for cyclohexane oxidation using *tert*-butyl hydroperoxide

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ABSTRACT

Many efforts have been made to develop new catalysts to oxidize cyclohexane under mild conditions. Herein, we report the effect of the X wt.-% Ru/Al_2O_3 on cyclohexane oxidation with tert-butyl hydroperoxide, to produce cyclohexanol and cyclohexanone. The catalysts were prepared using $Ru(C_5H_7O_2)_3$ as precursor and were characterized by chemical analysis, X.R.D., HRTEM, atomic absorption and BET. The oxidation reaction was carried at 341 K under atmospheric pressure. The catalysts were found to be highly efficient for such an oxidation type.

Keywords: Oxidation, Cyclohexane, Ruthenium, TBHP, Cyclohexanol, Cyclohexanone.

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INTRODUCTION

Functionalization of hydrocarbons by selective oxidation is a very useful reaction, of growing importance in modern chemical industry. Cyclohexane is oxidized to cyclohexanol and cyclohexanone, which are very important chemical intermediates since they are used as starting materials in the preparation of adipic acid and caprolactam, further used in the manufacture of nylon-6,6 and nylon-6 polymers. Worldwide production exceeds 10^6 ton per year. In addition, they are also used as solvent for lacquers, genizers for soaps and synthetic detergent emulsions. Normally, catalytic systems used for the industrial cyclohexane oxidation employs homogeneous catalysis using soluble transition metal salts such as (cobalt naphthenate or cobalt acetate), molecular oxygen and temperatures above 423K [1-3]. A low conversion (~ 4%) is obtained to avoid the formation of side products and to obtain a high selectivity (~ 85%) toward a mixture of cyclohexanone and cyclohexenol. Selective cyclohexane oxidation under mild conditions continues to be a challenge for chemists. On the other hand, for the laboratory-scale reactions extensive literature is available on the selective oxidation of cyclohexane using a variety of transition metal compounds in stochiometric amount as usual as homogenous catalysts [4-9]. Moreover, it is very difficult to separate the catalyst from the reaction mixture in the homogeneous system. Therefore, the development of effective recyclable solid catalysts could offer advantages. Various groups have illustrated the use of porous solids including the titanosilicate TS-1 [10-13], transition metal (Cr, V, Co, etc.) doped MCM-41 [14-18], oxides or metal cations incorporated in inorganic mixtures, such as silica, alumina, zirconia, active carbon, and zeolites [19-26] for the conversion.

Oxidation of organic substrates as catalyzed by coordination complexes of transition metals in resemblance of enzymatic oxidation is an intriguing area of current research [27-29]. In this regard, ruthenium complexes by virtue of their wide range of chemically accessible oxidation states have been the subject of many recent investigations [9, 30-31]. Ruthenium complexes have proved to be useful catalysts for the oxidation of organic substrates using molecular oxygen, iodosylbenzene and hypochlorite. However, the use of alkyl hydroperoxide is attractive in view of its ability toward the oxo-functionalization of aliphatic bond selectively in presence of ruthenium catalyst complexes [32]. Then Shun-Ichi Murahashi et al. [33] found that the ruthenium-catalyzed oxidation of alkanes with $^{tert-}$butyl hydroperoxide and peracetic acid produces the corresponding ketones and alcohols in a highly efficient manner at room temperature.

Thus, we undertook an investigation of cyclohexane oxidation with TBHP catalysed by Ru/Al_2O_3. In this paper, we report the impregnation synthesis of X wt.-% Ru/Al_2O_3, their characterization by various methods including chemical analysis, X-Rays Diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM), atomic absorption, and specific surface determination (BET) as well as their use as solid catalysts for cyclohexane oxidation using TBHP as oxidant.

EXPERIMENTAL

Synthesis of Ru/Al_2O_3

About 0.5; 1; 2 and 5 wt. % Ru catalysts supported on alumina were prepared as follow: The γ- alumina support was calcined in air for 4 hours at 400 °C prior to use. A dark red solution of $Ru(C_5H_7O_2)_3$ (Aldrich) in toluene was used to impregnate γ-Al_2O_3 (Fluka), particle size 100-125 µm, surface area 173 $m^2.g^{-1}$. After solvent evaporation, the impregnated products were dried at 393 K overnight. The samples were calcined under 20 % O_2 in N_2 at 350 °C for 4 hours and then reduced under H_2 flow at 350 °C for 4 hours.

Catalyst characterization

The effective content of Ru in the prepared catalysts was determined by chemical analysis at the Centre National de Recherche Scientifique (C.N.R.S.) in France. 0.5 and 5 % Ru/Al_2O_3 was analyzed. The principle of the used method is based on the dissolution of Ru by acid attack and then the analysis of the metallic ions by atomic absorption.

The dispersion of ruthenim was determined by H_2 chemisorption at room temperature. Metal surface areas and particle size were calculated assuming H/Ru = 1 and a Ru surface density equal to 1.2 10^{19} atoms.m^{-2}.

The X wt.-%Ru/Al_2O_3 (X = 0, 0.5, 1, 2, 5) have been characterized by X-Ray Diffraction (XRD) patterns for the samples were measured on a D5005 diffract meter equipped with a graphite monochromatic CuKα radiation (λ = 1.54060 nm) in the range of 2θ = 35°-150° with a step of 0.04° and acquisition time of 2 sec.

BET surface area was determined from N_2 adsorption-desorption at 77 K using FLOWSORB 2300 dynamic analyzer. Prior to the adsorption measurements, the sample was out-gazed at 623 K for 2 h under a flow of 30 % nitrogen in helium. Surface areas were automatically determined by the analyzer using the BET model.

Another important characterisation method of supported metal catalysts is the direct examination of the sample by high Resolution Transmission Electron Microscopy (HRTEM). TEM photographs were obtained from a TEM/STEM Philips CM120 instrument operating at 120KV with a resolution of 0.35 nm.

Catalytic cyclohexane oxidation reactions

Catalytic tests

Cyclohexane oxidation reactions were carried out in a 250 mL three-necked flask, placed in a temperature-equilibrated oil bath and fitted with reflux condenser. A solution of tert-butyl hydroperoxide (TBHP) in cyclohexane to be used as reaction mixture was prepared as follows: 8 mL of TBHP (70 % in aqueous solution - Aldrich) was mixed with 16 mL of cyclohexane (Fluka) in a closed Erlenmeyer flask and magnetically stirred for 24 hr. The organic phase was separated from the aqueous one, put in the three-necked flask and then heated to 343 K under vigorous agitation. Subsequently, 0.02 g of catalyst was added to the reaction mixture (time zero). The concentration of TBHP (99 %) in cyclohexane was determined by iodometric titration. The course of reactions was followed by gas chromatography (GC), tacking aliquots at different reaction times. A Schimadzu GC-14 B gas chromatograph equipped with an Apiezon L column (10 % on Chromosorb PUNDMCS) and a flame ionization detector (FID) was used. To such an end, 0.5 mL of sample was added to 0.04 mL of internal standard 1-Pentanol (Prolabo) and 0.3 μL of this sample was analysed.

Solvent effects

The organic phase prepared with a 1:1 ratio of cyclohexane and TBHP, as explain in paragraph II.3.1. was respectively added to different solvents (10 mL) such as methanol (Prolabo), acetic acid (Prolabo), acetonitrile (Prolabo) or dichloromethane (Prolabo).

RESULTS AND DISCUSSION

Characterization

The chemical analysis of the 0.5 and 5 % Ru/Al_2O_3 catalysts (table1) shows that practically 90 % of the impregnated ruthenium is truly deposited. These results can be extrapolated to the 1 and 2 % catalysts.

XRD patterns of the prepared catalysts are shown in figure 1. The XRD pattern of Al_2O_3 support is also given for refrence. The diffraction peaks at 44°, 78.5°, 84.8° and 86° 2θ correspond to crystalline Ru particles. No peaks attributed to Ru were observed for the 0.5 %Ru/Al_2O_3 due to the low content of the metal in this catalyst. The crystallite sizes calculated using the Ru peaks are listed in table 1.

The catalyst dispersion calculated for the 2 %Ru/ Al_2O_3 from H_2 chemisorption is 39 %. The particle size calculated from this dispersion is found to be 2.1 nm. This is in agreement with the particle distribution in which the majority size is 2.7 nm.

Analysis of HRTEM images of the Ru particles deposited on the alumina indicates a regular particle size distribution (figure 2). The Ru particles in the TEM are also consistent with the XRD results in which the average particle size is 10.8 nm. This particle size is comparable to the one obtained by Y. Han et al. [34]. In fact, based on the TEM imaging, they found that the low temperature reduction (LTR) pre-treatment, which involves reduction in pure H_2 at 423 K, does not lead to measurable particle growth (d_{Ru} = 2.5 nm), in contrast to the calcinations / reduction (CR) pre-treatment at 350 °C that was previously used, which lead to considerable particle sintering (d_{Ru} = 11.2 nm). However, the particle size distribution of the 5 %Ru/Al_2O_3 catalyst shows that the sizes are in the range of (8 – 16) nm. Y. Han et al. noted that particle sintering becomes more pronounced after higher temperature pre-treatments and in particular for the CR pre-treatment, as evidenced by the increase of the mean particle sizes to d_{Ru} = 5.5 ± 1.0 nm after 623 K reduction and to d_{Ru} = 11.2 ± 1.9 nm after the CR pre-treatment, respectively. As a consequence of the size particle increase, the dispersion decreases. Y. Han et al. found a D = 10.9 % for 5 %Ru/ Al_2O_3 catalyst.

Table 1 shows the results of surface area measurements by nitrogen adsorption at 77 K. It is noteworthy that the specific surface increases with the content of Ru, except for the 0.5 %Ru catalyst which has the highest area. In this case, we suppose that the alumina is involved in the specific surface area determination.

Catalytic test

Influence of metal content

The cyclohexane catalytic oxidation, with TBHP as oxidant, under reflux (70 °C), shows the cyclohexanol and cyclohexanone production. No oxidation is observed in the absence of the TBHP or the catalyst. Figure 3 depicts the effect of reaction time over X %Ru/Al_2O_3. It could be seen that the formation of the oxygenated products (ol + one) increases with time. Duly noted is 5 %Ru catalyst that gave the best production of the mixture (ol + one) (13 m.mol after 6 hours). S. I. Murahashi et al. [33] have studied the cyclohexane oxidation with TBHP and peracetic acid (CH_3CO_3H) over 5 %Ru/C. They found a (7.6 – 9.1) % the relative conversion of cyclohexane. From selectivity point of view, while the cyclohexanol selectivity varied between 4 – 5 % and that of cyclohexanone selectivity varied between 87 – 93 %.

All results of the reaction using the above catalysts are listed in the table 2. It could be seen that the cyclohexane conversion increases with the Ru content increase. Thus cyclohexanone and cyclohexanol are formed in 1:1 ratio for 0.5, 2 and 5 %Ru catalyst. In the other hand, for 1%Ru catalyst, the ketone to alcool ratio is 1 until 2 h of reaction and then increases with time suggesting that part of cyclohexanol is converted to cyclohexanone. P. Selvan et al. [20] found similar results with TiHMA. While cyclohexane conversion increases with the increase of titanium content in the catalyst, the selectivity toward cyclohexanol selectivity decreases. However the same results were observed by Lu et al. using Au/MCMW catalysts [35].

We have uses, in previous work, H_2O_2 (30 %) as oxidant with the same catalysts and in the same conditions. In this case, we observed an instant H_2O_2 decomposition when in contact of Ruthenium. Therefore, no reaction was possible.

Influence of solvent

Solvent plays an important and sometimes decisive role in catalytic behaviour because it could uniform different phases, thus promoting mass transportation. It could also change the reaction mechanism by affecting the intermediate species, the surface properties of the catalyst and reaction pathways [12]. Thus, the activity of the many oxidation systems is mainly based on the correct choice of the solvent, which determines the polarity of the medium and the substrate that needs to be adsorbed at the catalytic surface.

The effects of solvent on the catalytic activity of cyclohexane oxidation over 5 %Ru/Al_2O_3 are depicted in table 3.

Table 1: Characteristics X wt-%Ru/Al_2O_3

Samples	Ru content (%)	BET surface area (m^2/g)	Particle size by XRD (nm)	Particle size by HRTEM (nm)
0.5 wt.-%Ru/Al_2O_3	0.44	179.6	/	6.4
1 wt.-%Ru/Al_2O_3	/	149.5	11.1	8.3
2 wt.-%Ru/Al_2O_3	/	169.0	10.4	10.0
5 wt.-%Ru/Al_2O_3	4.35	173.3	11.2	8.2

Table 2: Results of cyclohexane oxidation over different Ru content catalysts.

Catalysts	Selectitity (%)		Turnover*
	One	Ol	($10^{-3}s^{-1}$)
0,5 wt.-%Ru	53.6	46.4	145
1 wt.-% Ru	64.6	35.4	127
2 wt.-% Ru	57.6	42.4	73
5 wt.-% Ru	53.5	46.5	61

C_6H_{12}: 148. m.mol, catalyst: 0.02 g, TBHP: 58.3 m.mol, T: 70 °C, reaction time: 6hr.
*Turnover: mole of substrate converted per mole of metal Ru in the catalyst per time.

Table 3: Oxidation of cyclohexane using various solvents over 5 %Ru/Al_2O_3

Solvent	Selectivity (%)		Turnover*
	Ol	One	($10^{-3}s^{-1}$)
Acetic acid	39.19	60.80	54
Dichloromethane	71.30	28.70	48
Cyclohexane	46.51	53.49	24
Methanol	48.51	51.49	12
Acetonitrile	42.60	57.40	11

C_6H_{12} : 58.3 m.mol, catalyst: 0.02 g, TBHP: 58.3 m.mol, Solvent: 10 mL, Reaction time: 6hr.
*Turnover: mole of substrate converted per mole of metal Ru in the catalyst per time.

Apparently this catalyst has the best performance in acetic acid. The higher catalytic activity in acetic acid compared to other solvents may be explained by supposing that acetic acid does not only act as a solvent, but also serves as a good oxidizing agent [13]. It can be seen from the table 3 that using acetic acid a solvent and 5 %Ru/Al_2O_3 as catalyst, cyclohexane would be oxidized into cyclohexanol and cyclohexanone in a 2:3 ratio with a good conversion (19.20 %). A. Bellifa et al. [36] explained their good conversion in acetic acid in a similar way. This solvent leads to the stabilisation of the peroxo band of HOOH as per acid according the following equation:

$$CH_3COOH + H_2O_2 \rightarrow CH_3CO_3H + H_2O$$

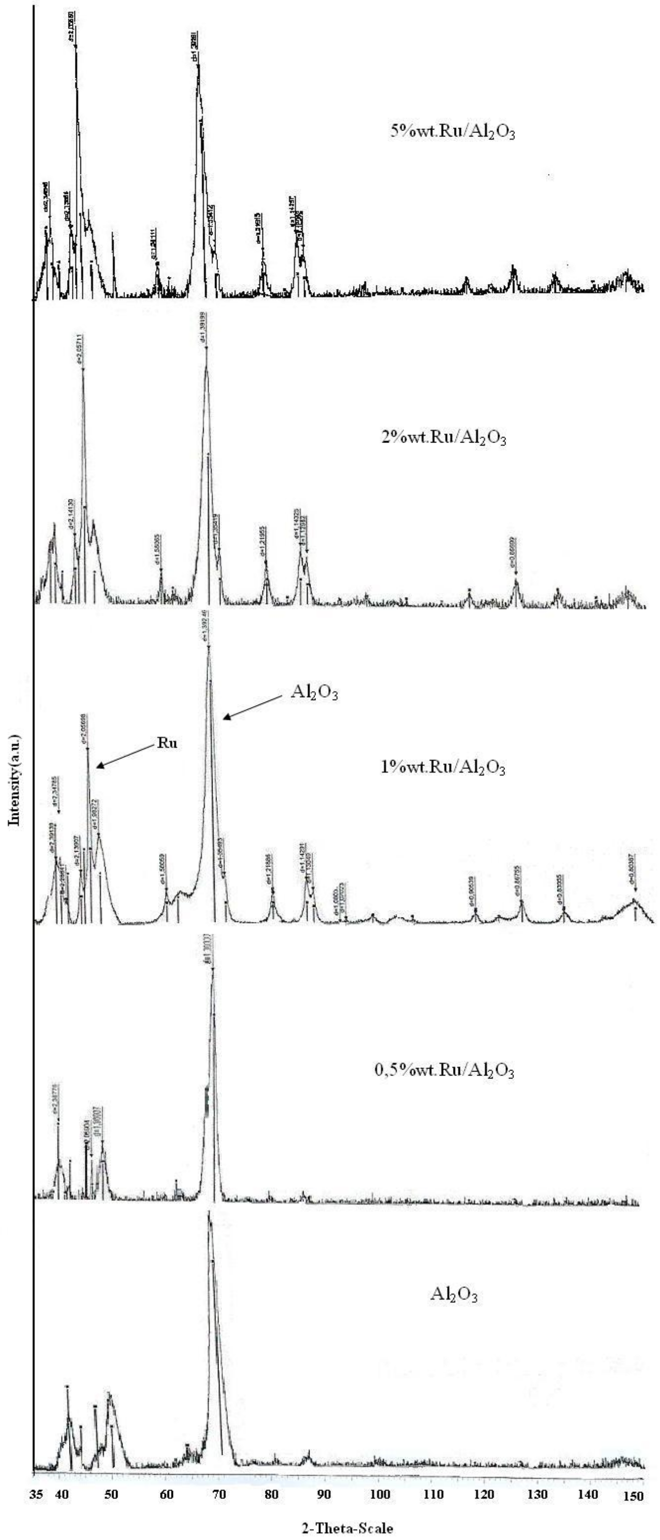

Fig.1. XRD patterns of Al_2O_3 and the X wt.-% Ru catalysts.

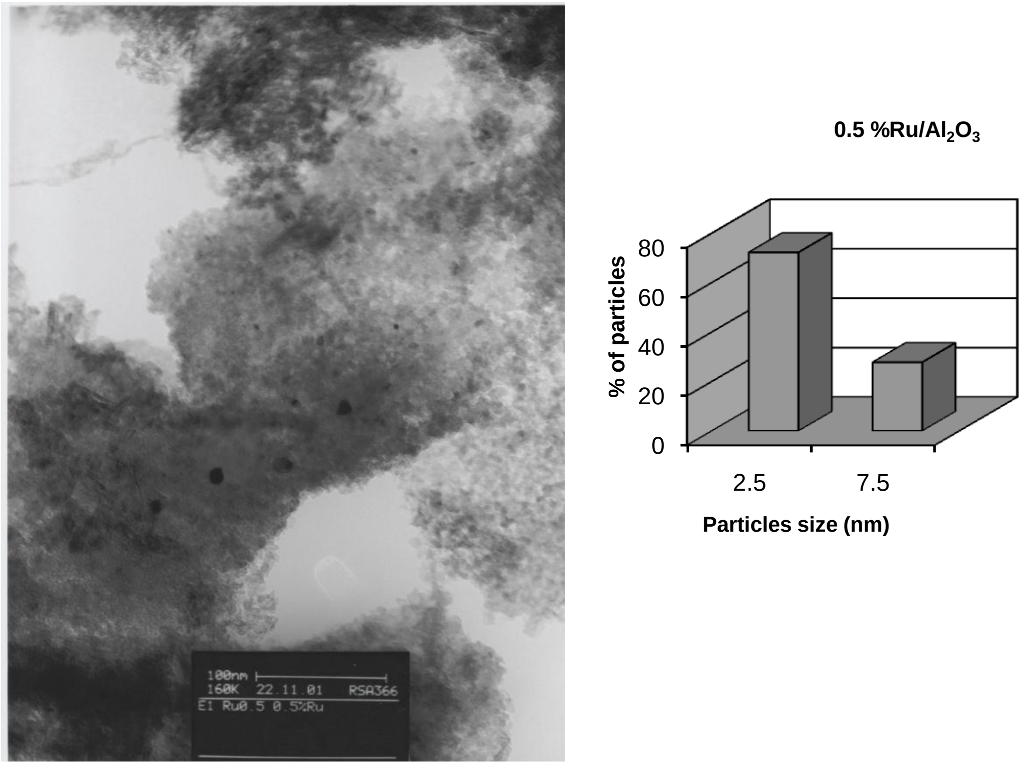

Fig. 2A. Representative High Resolution Transmission Electron Microscopy (HRTEM) images and particle size distribution of 0.5 %Ru.

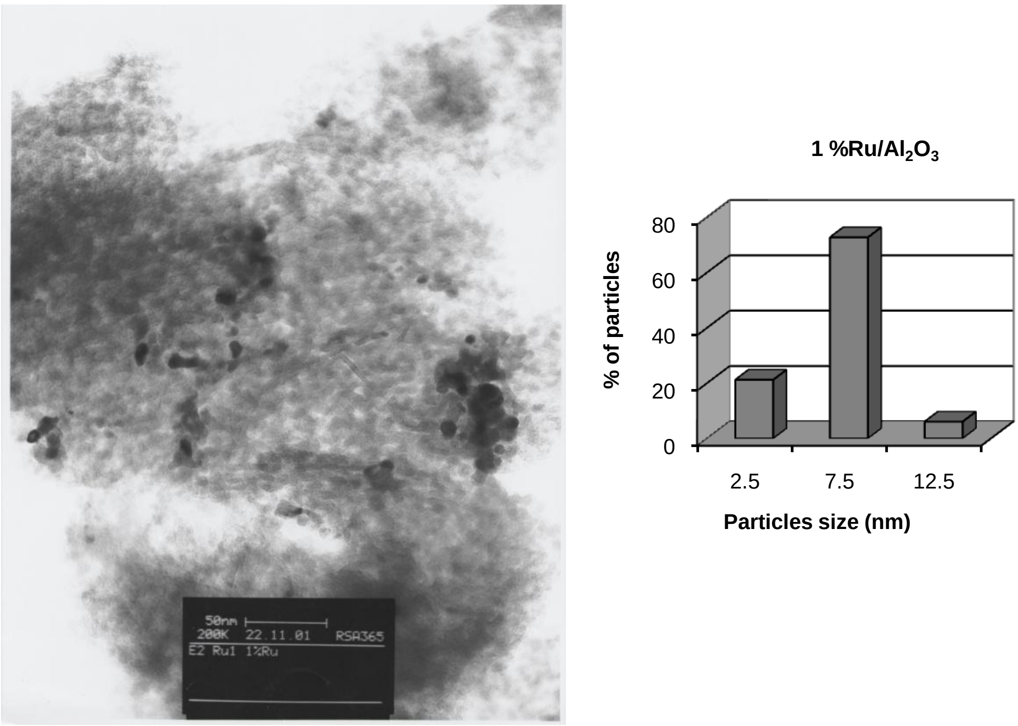

Fig. 2B. Representative High Resolution Transmission Electron Microscopy (HRTEM) images and particle size distribution of 1 %Ru.

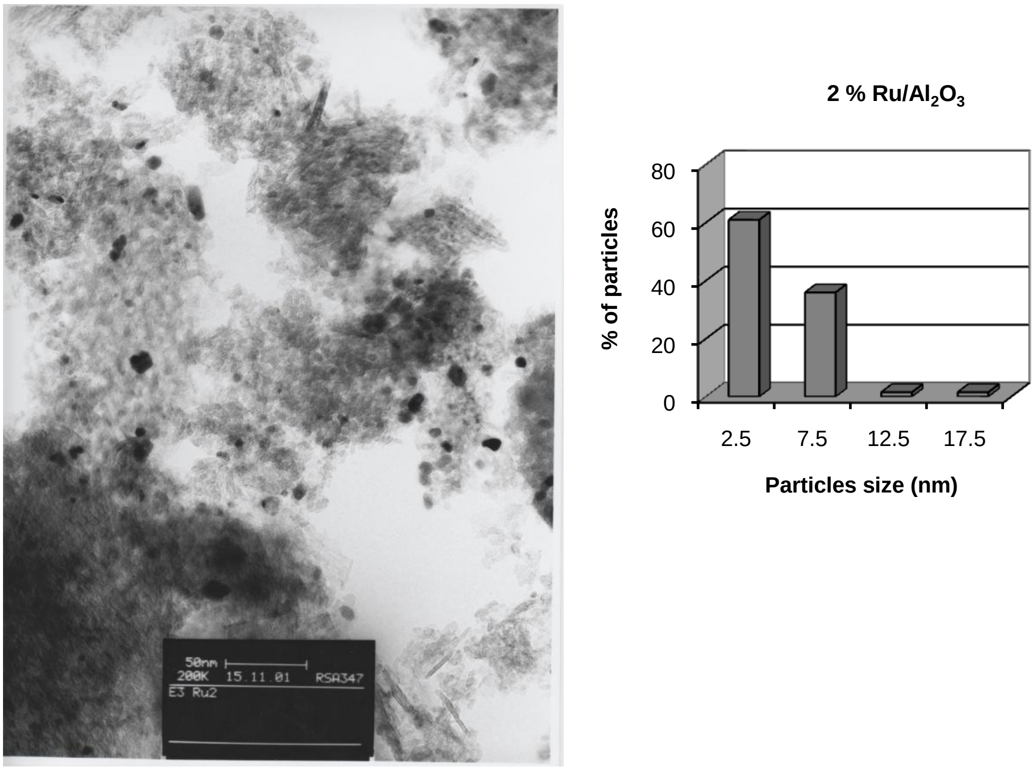

Fig. 2C. Representative High Resolution Transmission Electron Microscopy (HRTEM) images and particle size distribution of 2 %Ru.

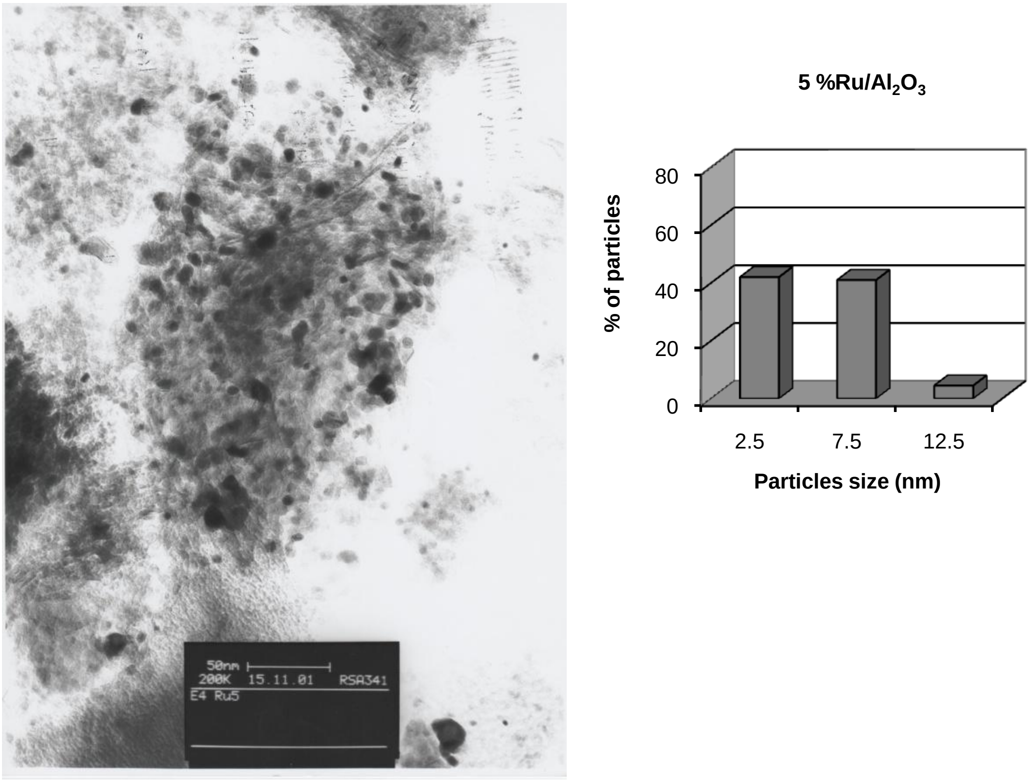

Fig. 2D. Representative High Resolution Transmission Electron Microscopy (HRTEM) images and particle size distribution of 5 %Ru.

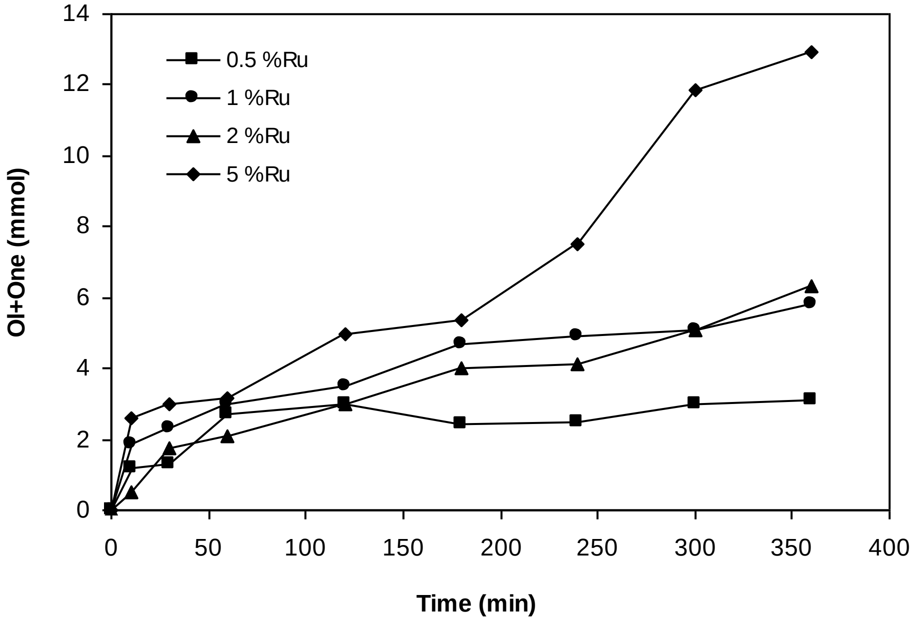

Fig. 3. Kinetics of oxidation of cyclohexane on X wt-%Ru/Al_2O_3 Catalysts.
Cyclohexane: 148.5 m.mol, catalyst: 0.02g, TBHP: 58.3 m.mol, T: 343 K, reaction time: 6hr.

Dichloromethane gives also a good conversion (18.28 %) and favours cyclohexanol formation (ol:one = 5:2). However, a relatively lower conversion was obtained in the case of acetonitril and methanol. P. Selvam et al. [20] have studies the effect of solvent in the oxidation of cyclohexane with TiHMA in presence of H_2O_2. They found that acetic acid lead to the higher conversion in contrast to methanol, acetonitrile and THF. W. Yao et al. [23] found a very good conversion (100 %) with a high selectivity (93.5 %) in presence of acid acetic using Co/TiO_2 as catalyst and H_2O_2 as oxidant.

CONCLUSION

The Ru catalysts were prepared and characterized by chemical analysis, X.R.D., HRTEM, atomic absorption and BET. We have demonstrated that supported Ru catalysts can be active and selective in the oxidation of cyclohexane using TBHP, to cyclohexanol and cyclohexanone with high conversions, when operated under mild conditions of temperature and pressure.

However, no results were obtained with H_2O_2 which decomposed instantaneously in the contact of Ruthenium. Among the various solvents, acetic acid was found to be the most suitable for the high conversion and high selectivity because it leads to the stabilization of the peroxo band of hydro peroxide as per acid.

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